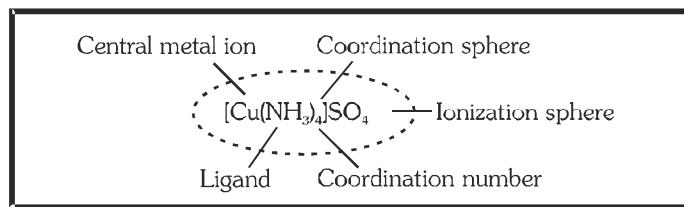


(d) Coordination Sphere - (Entity)

- (i) The central metal atom and the ligands directly attached to it are collectively termed as the coordination sphere.
- (ii) Coordination sphere is written inside square bracket, for example $[\text{Co}(\text{NH}_3)_6]^{3+}$
- (iii) The part outside the bracket is called **ionisation sphere**.
- (iv) The species present in the coordination sphere are non-ionisable.
- (v) The species present in the ionization sphere are ionisable.



(e) Oxidation State

It is a number which represents the electrical charge on the central metal atom of a complex ion.

Ex. the oxidation number of Fe, Co and Ni in $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $\text{Ni}(\text{CO})_4$ is +2, +3 and zero respectively.

(f) Charge On the Complex Ion

It is the algebraic sum of the total charge of the ligands and central metal ion.

(g) Ligands

- (i) The anions, cation or neutral molecules which combine with central metal ion to form complex ion are called as ligands.
- (ii) They act as electron pair donor (Lewis bases), but strong crystal field ligands like CO, CN^- etc can accept electron pair from the metal ion, because these ligands are π - acids.

(h) Naming of ligands

- (i) o-suffix is provided to the name of anionic ligands.
- (ii) ium-suffix is provided to the name of cationic ligands.

Classification of ligands :

On the basis of denticity :

1. Monodentate ligands : Which has only one donor site.

Neutral monodentate ligands	
NH_3	ammine
H_2O	aqua
NO	nitrosyl
PH_3	phosphine
PPh_3	triphenyl phosphine
O_2	dioxygen
N_2	dinitrogen
$\text{CH}_3\text{-OH}$	methyl alcohol
$\text{CH}_3\text{-NH}_2$	methyl amine
NH_2CONH_2	urea
NH_2NH_2	hydrazine
$\text{CH}_3\text{-O-CH}_3$	dimethyl ether
CO	carbonyl
CS	thiocarbonyl



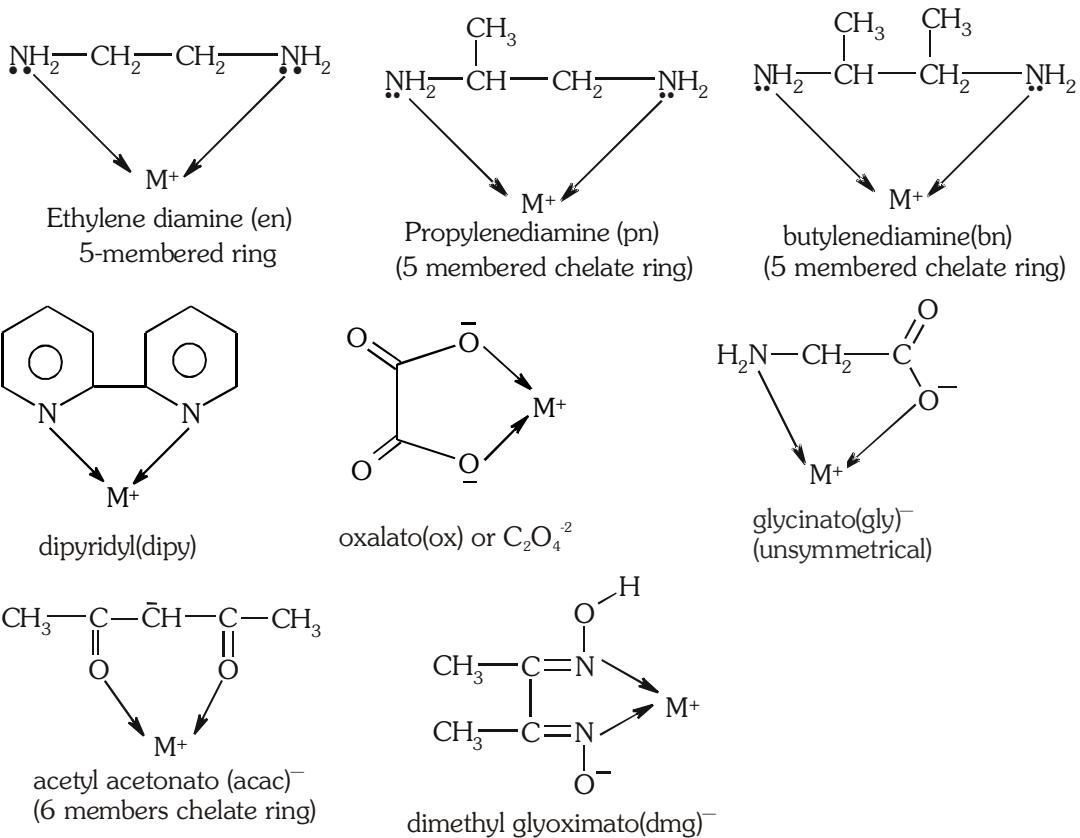
Cationic monodentate ligands :

O_2^+	oxygenium
NO^+	nitrosylum or nitrosonium
NO_2^+	nitronium
$H_2N - \overset{+}{NH}_3$	hydrazinium

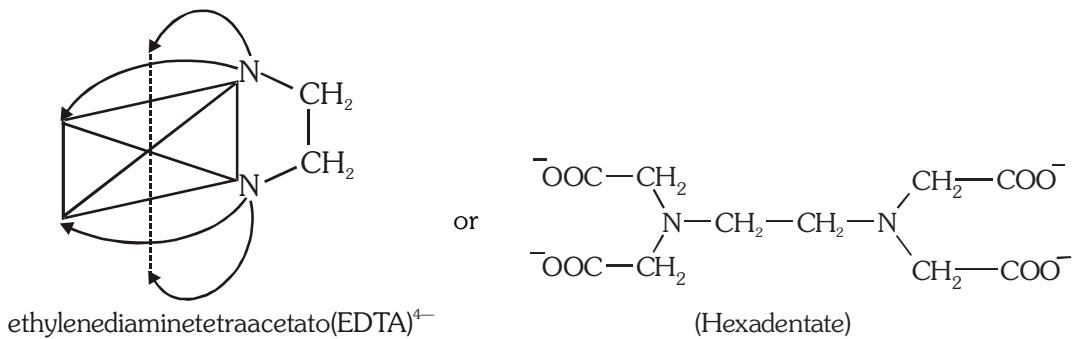
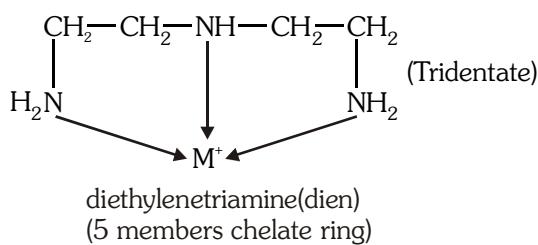
Anionic monodentate ligands :

F^-	Fluorido / fluoro
Cl^-	Chlorido / chloro
Br^-	bromido / bromo
I^-	iodido / iodo
O^{2-}	oxido/oxo
S^{2-}	sulphido/sulpho
OH^-	hydroxido / hydroxo
$CH_3 - O^-$	methoxido / methoxo
O_2^-	superoxido / superoxo
O_2^{2-}	peroxido / peroxy
N^{3-}	nitrido
N_3^-	azido
$(NH_2)_2^-$	amido
NH^{2-}	imido
H^-	hydrido

2. Bidentate ligands : Ligands which has two donor sites (simultaneously)



3. Polydentate ligands



4. **Ambidentate ligand :** Ligands which have two different donor atoms but at the time of coordination can donate electron pair from any one donor atoms are called ambidentate ligand.

(i)	$\text{M} \leftarrow \bar{\text{C}} \equiv \text{N}$	cyanido (CN^-)
	$\text{M} \leftarrow \text{N} \equiv \bar{\text{C}}$	isocyanido(NC^-)
(ii)	$\text{M} \leftarrow \bar{\text{O}} - \text{C} \equiv \text{N}$	cyanato / cyanato-O
	$\text{M} \leftarrow \text{N} \equiv \text{C} - \bar{\text{O}}$	isocyanato / cyanato-N
(iii)	$\text{M} \leftarrow \bar{\text{S}} - \text{C} \equiv \text{N}$	Thiocyanato / Thiocyanato-S
	$\text{M} \leftarrow \text{N} \equiv \text{C} - \bar{\text{S}}$	Isothiocyanato/thiocyanato-N
(iv)	$\text{M} \leftarrow \bar{\text{O}} - \text{N} = \text{O}$	Nitrito / Nitrito-O
	$ \begin{array}{c} \text{M} \leftarrow \text{N} \\ \\ \text{O} \\ \\ \text{O}^- \end{array} $	Nitro / Nitrito-N

5. **Flexidentate ligands :** Ligands which can change their denticity.

SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, CO_3^{2-} , NO_3^- , CH_3COO^- etc are generally act as monodentate ligand but in some compound they can act as bidentate ligand

eg. (i) $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Cl}$ in this complex SO_4^{2-} act as a monodentate ligand.

(ii) $[\text{Co}(\text{en})_2(\text{SO}_4)]\text{Cl}$ in this complex SO_4^{2-} act as a bidentate ligand.

6. **Chelating ligands :** Bidentate or polydentate ligands which attach themselves with central metal ion in such a way that they form a ring, are known as chelating ligands.

No. of rings = denticity - 1

5 or 6 membered rings are more stable

e.g. (i) $[\text{Pt}(\text{trien})]\text{SO}_4$ (ii) $\text{Na}_2[\text{Fe}(\text{OH})(\text{EDTA})]$
denticity = 4 denticity of EDTA = 5
chelating rings = 3 chelating rings = 4



On the basis of nature of bonding between central metal atom and ligand.

(i) Normal or classical ligands :

Ligand which only donate electron pair to central metal ion & form coordinate (σ) bond
e.g. OH^- , NH_2^- , Cl^- , N^{3-} , O^{2-} etc.

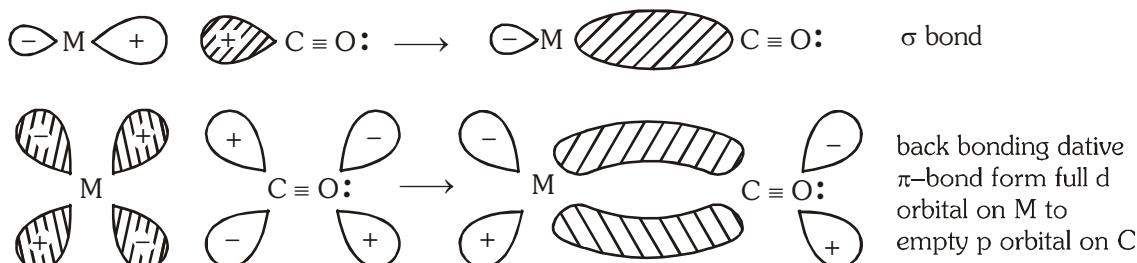
(ii) Non classical or π -acid or π -acceptor ligands :

Ligand which donate electron pair to central metal ion & form coordinate σ bond but simultaneously they accept electron pair from central metal ion through back bonding or synergic bonding.

CO , NO^+ , CN^- , R_3P , R_3As etc.

The electronic configuration of CO molecule shows that it has lone pair of electrons on carbon and oxygen atom each. Carbon atom can donate its electron pair of a transition metal atom (M), forming $\text{OC} \rightarrow \text{M}$ coordinate bond.

Since the metal atom in metal carbonyl is in zero oxidation state, the formation of $\text{M} \leftarrow \text{CO}$ σ bond accumulates a negative charge on the metal atom. The accumulation of negative charge on the metal atom can be counter balanced by transferring some negative charge from the metal atom to CO molecule (ligand). This transfer can be done by making a $\text{M} \rightarrow \text{CO}$ π bond by the overlap between an appropriate filled orbital on the metal atom and empty π_y^* or π_z^* molecular orbital on CO molecule. This type of bonding between M and CO is called **synergic bonding**.



[Schematic of orbital overlaps in metal carbonyls]

Conclusion of synergic bonding : due to synergic bonding

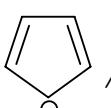
- (a) M-C bond strength increases; M-C bond length decreases; because double bond character increases
- (b) C-O bond strength decreases; C-O bond length increases; because bond order of C-O decreases, electron density in ABMO of CO increases.

π -donor and π -acceptor ligands

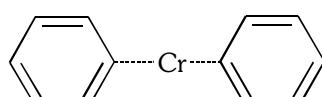
Ligands which donate π electron to central metal ion & also accept electron density from central metal ion through synergic bonding.

(i) $\text{H}_2\text{C}=\text{CH}_2$ (η^2 - ethylene) : it is a 2π electron donor

(ii)  (η^6 - benzene) : it is a 6π electron donor

(iii)  / $[\text{C}_5\text{H}_5^-]$ (η^5 - cyclopentadienyl) : it is a 6π electron donor

for example



(a) $[\text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2]$

sandwich compound

(b) $[\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2]$

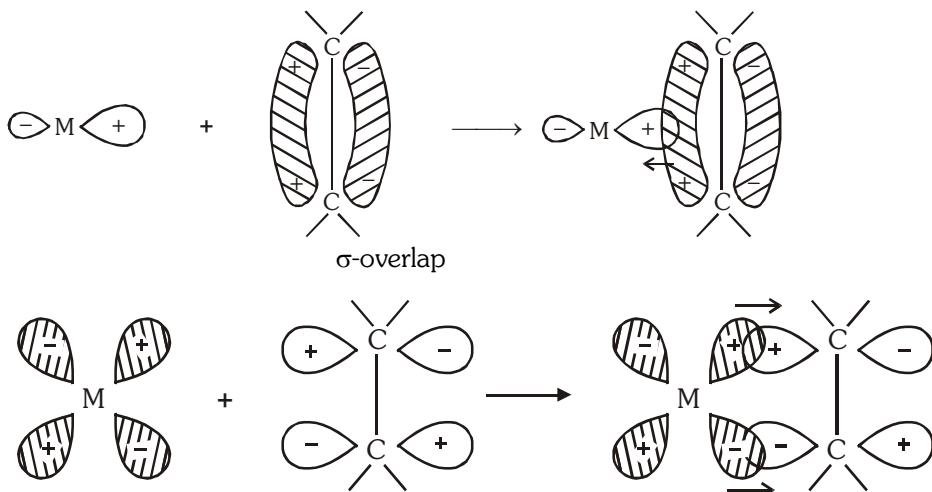
ferrocene (sandwich compound)

(c) $\text{K}[\text{PtCl}_3(\eta^2-\text{C}_2\text{H}_4)]$

(Zeise's salt)



The bonding of alkenes to a transition metal to form complexes has two components. First, the π -electron density of the alkene overlaps with a σ -type vacant orbital of the metal atom. Second is the back bonding formed by the flow of electron density from a filled d-orbital on the metal into the vacant π^* -antibonding molecular orbital of the carbon atom as shown below:



BEGINNER'S BOX-1

- Which of the following is true about metal-EDTA complex (if it is a 3d metal)
 - The ratio of moles of metal & EDTA in complex is 1:6
 - The ratio of moles of metal & EDTA in complex is 6:1
 - The ratio of moles of metal & EDTA in complex is 1:1
 - 3d metal ion cannot bond with EDTA
- CN^- is ambidentate ligand because

(1) it has multiple bonds	(2) carbon as a negative charge
(3) it forms chelate	(4) both C & N can donate lone pair
- Highest C–O bond length will be in

(1) $[\text{Mn}(\text{CO})_6]^+$	(2) $[\text{Cr}(\text{CO})_6]$	(3) $[\text{V}(\text{CO})_6]^-$	(4) same in all
----------------------------------	--------------------------------	---------------------------------	-----------------
- The strongest –CO bond is present in

(1) $[\text{Cr}(\text{CO})_6]^+$	(2) $[\text{Fe}(\text{CO})_5]$	(3) $[\text{V}(\text{CO})_6]^-$	(4) all have equal strength
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5. Match the following

Ligand

(A) ethylenediamine
 (B) hydrazene
 (C) dimethylglyoximato(dmg)
 (D) dien

Property

(P) bidentate
 (Q) tridentate
 (R) form hydrazinium ion on protonation
 (S) can form dimer

[Ans. A \rightarrow P, B \rightarrow R, C \rightarrow P, D \rightarrow Q]

6. Match the following

Complex

(A) $[\text{Ni}(\text{dmg})_2]$
 (B) $[\text{Ca}(\text{EDTA})]^{2-}$
 (C) $[\text{Fe}(\text{en})_3]\text{Cl}_3$
 (D) $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$

Property

(P) number of 5 member rings = 2
 (Q) number of 6 member rings = 2
 (R) coordination number of central metal ion = 2
 (S) coordination number of central metal ion = 6
 (T) intramolecular H-bonding

[Ans. A \rightarrow P, Q, T; B \rightarrow S; C \rightarrow S; D \rightarrow R]



3.2 IUPAC NOMENCLATURE OF COORDINATION COMPOUNDS

The present system of nomenclature derived from the suggestions of **Alfred Werner** and recommended by the Inorganic Nomenclature Committee of the I.U.P.A.C. The main rules of naming of complexes are -

(a) Like simple salts, the positive part of the coordination compound is named first.

Ex. $K_4[Fe(CN)_6]$ the naming of this complex starts with potassium.

(b) Then after ligands of the coordination sphere are to be named.

(c) The ligands can be neutral, anionic or cationic.

(i) The neutral ligands are named as the molecule.

Ex. C_6H_5N (pyridine), $(C_6H_5)_3P$ (Triphenyl phosphine).

$\text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$ (ethylene diamine)

The neutral ligands which are not named as the molecule are

CO (carbonyl), NO (nitrosyl), H₂O (Aqua), NH₃ (ammine)

(ii) Anionic ligands ending with 'ide' are named by replacing the 'ide' with suffix 'O'.

Symbol	Name as ligand	Symbol	Name as ligand
Cl^-	Chloro/Chlorido	N^{3-}	Nitrido
Br^-	Bromo/Bromido	O_2^{2-}	Peroxo, O_2^- superoxo
CN^-	Cyano	O_2H^-	Perhydroxo
O^{2-}	Oxo	S^{2-}	Sulphido
OH^-	Hydroxo	NH_2^-	Amido
H^-	Hydrido	NH^{2-}	imido

Ligands whose names end in 'ite' or 'ate' become 'ito' i.e., by replacing the ending 'e' with 'o' as follows.

CO_3^{2-}	Carbonato	SO_3^{2-}	Sulphito
$\text{C}_2\text{O}_4^{2-}$	Oxalato (Ox) ²⁻	CH_3COO^-	Acetato
SO_4^{2-}	Sulphato	NO_2^-	(bonded through oxygen) nitrite
NO_3^-	Nitrato		(bonded through nitrogen) nitro

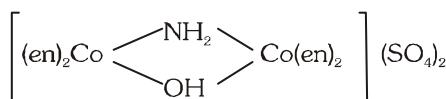
(iii) Positive ligands naming ends in 'ium'

$\text{NH}_2-\text{NH}_3^+$ (Hydrazinium), NO_2^+ (nitronium); NO^+ (nitrosonium)

(d) If ligands are present more than once, then their repetition is indicated by prefixes like di, tri, tetra etc. However, when the name of the ligand includes a number.

Ex. dipuridyl, ethylene diamine, then bis, tris, tetrakis are used in place of di, tri, tetra, etc.

(e) In case of chelating ligands or ligands having di, tri, tetra, etc, in their name the prefixes bis, tris, tetrakis are used before ligands placed in parenthesis.



Bis(ethylenediamine) cobalt(III)- μ - amido- μ - hydroxobis(ethylenediamine) cobalt (III) sulphate

(f) When more than one type of ligand is present in the complex, then the ligands are named in the alphabetical order.

(g) After naming of ligands the central metal ion is to be named followed by its oxidation state in Roman numbers in brackets. (as per IUPAC)

If the complex is neutral or provides a cationic complex ion, then the central metal ion is to be named as it is.

If the complex provides anionic complex ion then the name of central metal ion ends in 'ate'

(h) After the naming of central metal ion, anion which is in the outer sphere is to be named.

The naming of some of the complexes is done as follows – (as per IUPAC)

Complex Compounds	IUPAC Name
(i) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (anionic complex) so suffix ate is added with metal's name	Potassium hexacyanidoferate (II)
(ii) $\text{K}_2[\text{Pt Cl}_6]$	Potassium hexachloridoplatinate (IV)
(iii) $[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$ (Cationic complex) so metal is without any suffix	Hexamminecobalt (III) chloride
(iv) $[\text{Cr}(\text{H}_2\text{O})_4 \text{Cl}_2] \text{Cl}$	Tetraaquadichlorochromium (III) chloride
(v) $[\text{Pt}(\text{NH}_3)_2 \text{Cl}_4]$	Diammine tetrachloroplatinum (IV)
(vi) $[\text{Co}(\text{NH}_3)_3 \text{Cl}_3]$ (Neutral complex) So no suffix is used with metal ion	Triamminetrichlorocobalt (III)
(vii) $\text{K}_3[\text{Co}(\text{NO}_2)_6]$	Potassium hexanitrocobaltate (III)
(viii) $\text{Na}_2[\text{Fe}(\text{CN})_5 \text{NO}]$	Sodium pentacyanonitrosoniumferrate (II)
(ix) $[\text{NiCl}_4]^{2-}$	Tetrachloronickelate (II) ion
(x) $[\text{Ru}(\text{NH}_3)_5 \text{Cl}]^{+2}$	Pentamminechlororuthenium (III) ion
(xi) $[\text{Fe}(\text{en})_3] \text{Cl}_3$	Tris (ethylenediamine) iron (III) chloride
(xii) $[\text{Ni}(\text{Gly})_2]$	Bis (glycinato) nickel (II)

(i) If coordination compound contains 2 coordination spheres then both spheres should have opposite charges. Name of cationic part written first following the name of anionic sphere according to the general IUPAC rule.

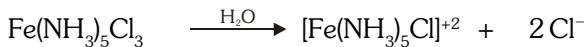
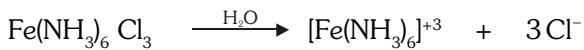
Ex. $[\text{Fe}(\text{NH}_3)_6]_3[\text{Co}(\text{NO}_2)_6]_2$ [Hexaamine iron (II) hexanitro cobaltate(III)]



3.3 BONDING IN COORDINATION COMPOUNDS

(A) Werner's Theory

This was postulated by **Alfred Werner** in 1893. The postulates of Werner's theory of complexes are –



Every metal forming a complex exhibits two types of valencies - Primary valency and Secondary Valency. In the above complexes chlorine act as primary valency and NH_3 acts as secondary valency.

According to Werner central metal have 2 types of valencies :

Primary valencies	Secondary valencies
(i) Equal to oxidation state of CMA	(i) Equal to coordination number of CMA
(ii) Satisfied by anions	(ii) satisfied by ligands
(iii) Non directional	(iii) Directional
(iv) Ionisable	(iv) Non-ionisable
(v) not helpful geometry predictions	(v) helpful in geometry predictions

Shapes : According to Werner all secondary valencies has shapes arrangement according to coordination number

Experimental evidence of werner's theory

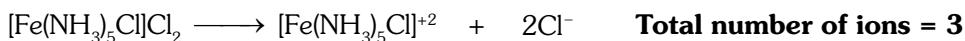
(a) Precipitation of primary valencies on the addition of a suitable reagent.

Ex. $\text{Fe}(\text{NH}_3)_6 \text{Cl}_3$ forms 3 moles of AgCl in the form of precipitate on addition of AgNO_3 solution.

This indicates that the complex ionises as $\text{Fe}(\text{NH}_3)_6 \text{Cl}_3 \xrightarrow{\text{H}_2\text{O}} [\text{Fe}(\text{NH}_3)_6]^{+3} + 3 \text{Cl}^-$

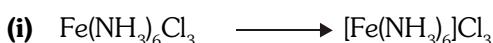
(b) **Electrical conductance of complexes** : More the number of ions provided greater is the electrical conductance of the complex in aqueous medium. **Electrical conductivity \propto no. of ions.**

Ex. The electrical conductance of aqueous $[\text{Fe}(\text{NH}_3)_6] \text{Cl}_3$ is greater than that of aqueous solution of $[\text{Fe}(\text{NH}_3)_5 \text{Cl}] \text{Cl}_2$.

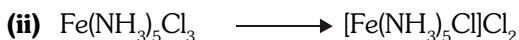
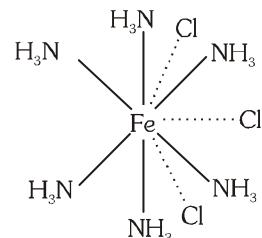


Complex	Modern formula	No. of Cl^- ions precipitated	Total number of ions
$\text{PtCl}_4 \cdot 6\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_6] \text{Cl}_4$	4	5
$\text{PtCl}_4 \cdot 5\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_5 \text{Cl}] \text{Cl}_3$	3	4
$\text{PtCl}_4 \cdot 4\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_4 \text{Cl}_2] \text{Cl}_2$	2	3
$\text{PtCl}_4 \cdot 3\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_3 \text{Cl}_3] \text{Cl}$	1	2
$\text{PtCl}_4 \cdot 2\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_2 \text{Cl}_4]$	0	0 (non-electrolyte)

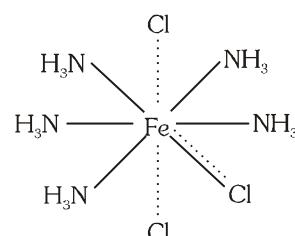
Werner's Representation of complexes

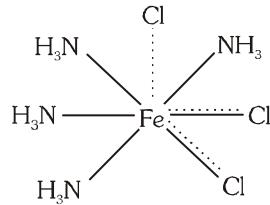
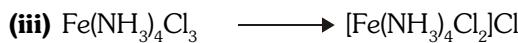


Dotted lines indicate primary valency and continuous lines indicate secondary valency of metal ion.



In this complex 'Cl' groups act as primary valencies and one of the 'Cl' acts as secondary valency also. Thus werner's representation of this complex –





In this complex 'Cl' groups act as primary valency and two of the 'Cl' group act as secondary valencies also. Thus Werner's representation of this complex –

E.A.N. = (No. of electron in the metal ion) + (No. of electrons gained from the ligands)

OR

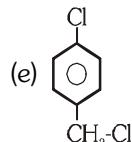
Atomic number – (Oxidation state) + (2 × Coordination number)

Example :

Complex	Metal	Atomic	Coordination	Effective atomic number
	(Oxidation State)	Number of Metal	number	(E.A.N.)
$[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$	+2	29	4	$(29 - 2) + (4 \times 2) = 35$
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	+3	27	6	$(27 - 3) + (6 \times 2) = 36$ [Kr]
$\text{K}_2[\text{HgI}_4]$	+2	80	4	$(80 - 2) + (4 \times 2) = 86$ [Rn]
$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$	+1	47	2	$(47 - 1) + (2 \times 2) = 50$

BEGINNER'S BOX-2

(d) Vinyl chloride



(f) Carnallite

(1) a, c, f, e

(2) a, d, e

(3) a, b, c, f

(4) a, b, e, f

6. Which of the following is most likely formula of platinum complex, if $\frac{1}{4}$ of total chlorine of the compound is precipitated by adding AgNO_3 to its aqueous solution

(1) $\text{PtCl}_4 \cdot 6\text{H}_2\text{O}$ (2) $\text{PtCl}_4 \cdot 5\text{H}_2\text{O}$ (3) $\text{PtCl}_2 \cdot 2\text{H}_2\text{O}$ (4) $\text{PtCl}_4 \cdot 3\text{H}_2\text{O}$

7. The Effective atomic number of Cr in $\text{Cr}(\text{CO})_6$ is

(1) 36 (2) 38 (3) 28 (4) 54

8. According to the rule of effective atomic number, central atom acquires :

(1) Inert gas configuration (2) Duplet
 (3) Pseudo inert electronic configuration (4) Quartet

9. The Effective atomic number of iron in $\text{K}_4[\text{Fe}(\text{CN})_6]$ is :

(1) 35 (2) 34 (3) 36 (4) 38

10. The formula of the complex tris (ethylene diamine) cobalt (III) sulphate is

(1) $[\text{Co}(\text{en})_2\text{SO}_4]$ (2) $[\text{Co}(\text{en})_3\text{SO}_4]$ (3) $[\text{Co}(\text{en})_3]\text{SO}_4$ (4) $[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$

(B) VALENCE BOND THEORY

This theory was mainly developed by **Linus Pauling**. The main features of this theory are -

- (a) Every metal ion when it forms a complex compound undergoes formation of coordinate covalent bond.
- (b) During this bond formation, the metal ion acts as electron pair acceptor. For this the metal ion provides vacant orbitals.
- (c) The number of vacant orbitals provided is equal to the coordination number of metal ion.

Ex. In the formation of $[\text{Fe}(\text{NH}_3)_6]^{3+}$, Fe^{3+} ion provides six vacant orbitals.

In $[\text{Cu}(\text{NH}_3)_4]^{2+}$, Cu^{2+} ion provides four vacant orbitals.

- (d) The metal provides vacant orbitals only after the process of hybridisation, thus vacant hybrid orbitals are provided by the metal ion.
- (e) The vacant hybrid orbitals of metal ion get overlapped by orbitals of ligands containing lone pair of electrons.
- (f) The number of such overlappings is equal to the coordination number of metal ion.
- (g) The empty 'd' orbitals involved in hybridisation may be inner $(n-1)d$ or outer "nd" orbitals.
- (h) These complexes are called as **Inner orbital complexes** and **outer orbital complexes** respectively. It is applicable for coordination number = 6 (complexes).
- (i) If inner 'd' orbitals are involved in hybridisation, then it is through the pairing of unpaired electrons in the $(n-1)d$ orbitals of metal ion.
- (j) Then such type of complexes will be **diamagnetic** or **less paramagnetic** and will be called as **Low spin complexes**.
- (k) Generally outer orbital complexes have **paramagnetic** nature and they are called as **High spin complexes**.



Applications of valence bond Theory

(a) To 6-coordinated complexes :



e^- configuration of ${}_{27}\text{Co} = [\text{Ar}] 3d^7 4s^2$ So, $\text{Co}^{+3} = [\text{Ar}] 3d^6$

Co^{3+}	<table border="1"> <tr><td>1/</td><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td></tr> </table>	1/	1	1	1	1	1	<table border="1"> <tr><td></td></tr> </table>		<table border="1"> <tr><td></td><td></td><td></td></tr> </table>				<table border="1"> <tr><td></td><td></td><td></td><td></td></tr> </table>				
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	3d	4s	4p	4d														

Due to presence strong ligand electrons get paired up so metal ion provides vacant '3d' orbitals for hybridisation.

Co^{+3} in $[\text{Co}(\text{NH}_3)_6]^{3+}$	<table border="1"> <tr><td>1/</td><td>1/</td><td>1/</td><td></td></tr> </table>	1/	1/	1/		<table border="1"> <tr><td></td></tr> </table>		<table border="1"> <tr><td></td><td></td><td></td></tr> </table>				<table border="1"> <tr><td></td><td></td><td></td><td></td></tr> </table>				
1/	1/	1/														
	3d	4s	4p	4d												
d^2sp^3 hybridisation																

- This is a **diamagnetic complex**.
- As inner 'd' orbitals are involved in hybridisation, hence it is an **inner orbital complex**.
- It is a **low spin complex**.



Co^{27}	<table border="1"> <tr><td>1/</td><td>1/</td><td>1</td><td>1</td><td>1</td><td>1</td></tr> </table>	1/	1/	1	1	1	1	<table border="1"> <tr><td>1/</td></tr> </table>	1/	<table border="1"> <tr><td></td><td></td><td></td></tr> </table>				<table border="1"> <tr><td></td><td></td><td></td><td></td></tr> </table>				
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Co^{3+} ion	<table border="1"> <tr><td>1/</td><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td></tr> </table>	1/	1	1	1	1	1	<table border="1"> <tr><td></td></tr> </table>		<table border="1"> <tr><td></td><td></td><td></td></tr> </table>				<table border="1"> <tr><td></td><td></td><td></td><td></td></tr> </table>				
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Co^{+3} in $[\text{CoF}_6]^{3-}$	<table border="1"> <tr><td>1/</td><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td></tr> </table>	1/	1	1	1	1	1	<table border="1"> <tr><td></td></tr> </table>		<table border="1"> <tr><td></td><td></td><td></td></tr> </table>				<table border="1"> <tr><td></td><td></td><td></td><td></td></tr> </table>				
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	3d	4s	4p	4d														
sp^3d^2																		

- This is a **paramagnetic** complex and **high spin** complex.
- The outer 'd' orbitals are involved in hybridisation, hence it is an **outer orbital** complex.



Co^{27}	<table border="1"> <tr><td>1/</td><td>1/</td><td>1</td><td>1</td><td>1</td><td>1</td></tr> </table>	1/	1/	1	1	1	1	<table border="1"> <tr><td>1/</td></tr> </table>	1/	<table border="1"> <tr><td></td><td></td><td></td></tr> </table>				<table border="1"> <tr><td></td><td></td><td></td><td></td></tr> </table>					
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Co^{+2} in $[\text{Co}(\text{NH}_3)_6]^{2+}$	<table border="1"> <tr><td>1/</td><td>1/</td><td>1/</td><td></td><td></td><td></td></tr> </table>	1/	1/	1/				<table border="1"> <tr><td></td></tr> </table>		<table border="1"> <tr><td></td><td></td><td></td></tr> </table>				<table border="1"> <tr><td>1</td><td></td><td></td><td></td><td></td></tr> </table>	1				
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	3d	4s	4p	4d															
d^2sp^3																			

(b) 4-coordinated complexes :



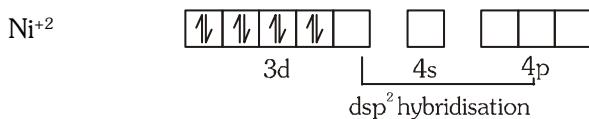
Ni^{+2}	<table border="1"> <tr><td>1/</td><td>1/</td><td>1/</td><td>1</td><td>1</td><td>1</td></tr> </table>	1/	1/	1/	1	1	1	<table border="1"> <tr><td></td></tr> </table>		<table border="1"> <tr><td></td><td></td><td></td></tr> </table>			
1/	1/	1/	1	1	1								
	3d	4s	4p										

- The unpaired electrons remain as such because Cl^- is a weak ligand as it is a **paramagnetic complex**.

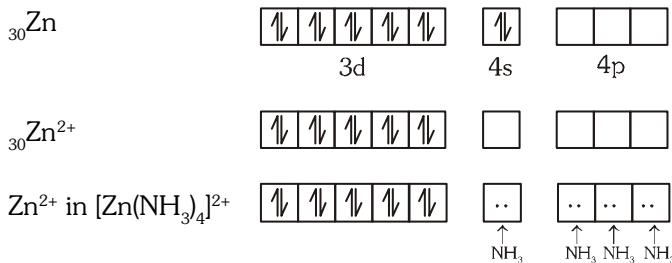
Ni^{2+} in $[\text{NiCl}_4]^{2-}$	<table border="1"> <tr><td>1/</td><td>1/</td><td>1/</td><td>1</td><td>1</td><td>1</td></tr> </table>	1/	1/	1/	1	1	1	<table border="1"> <tr><td></td></tr> </table>		<table border="1"> <tr><td></td><td></td><td></td></tr> </table>			
1/	1/	1/	1	1	1								
	3d	4s	4p										
sp^3 hybridisation													



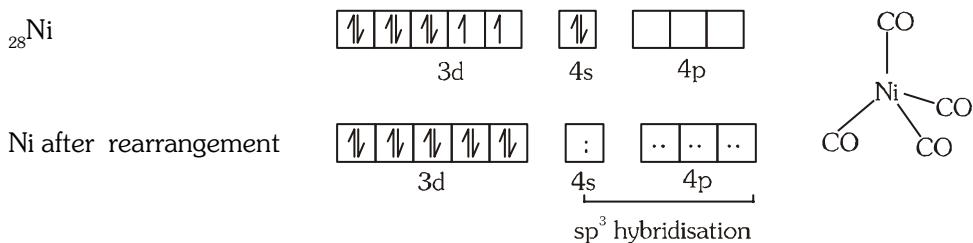
- $[\text{NiCl}_4]^{2-}$ has **tetrahedral geometry**.
- It is a **high spin complex**.



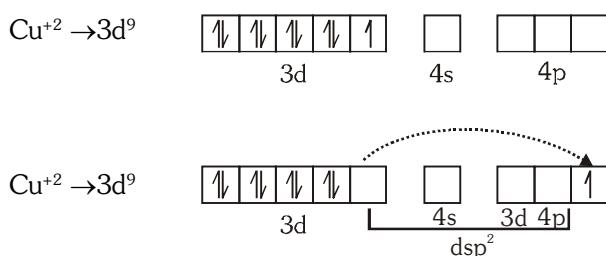
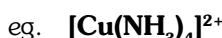
- CN^- is **strong field ligand**. Thus the complex has **square planar geometry**.
- The unpaired electrons in '3d' orbitals of Ni^{+2} get paired up, So $[\text{Ni}(\text{CN})_4]^{2-}$ is **diamagnetic** in nature.
- This Ni^{+2} complex is an **inner orbital complex** and a **low spin complex**.



- Because the complex is formed by sp^3 hybridisation, hence it is **tetrahedral**
- Since all electrons are paired, hence it is **diamagnetic**



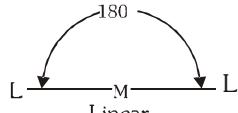
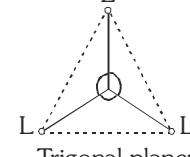
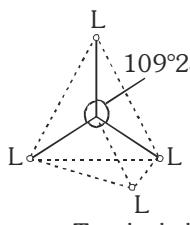
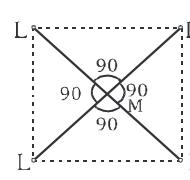
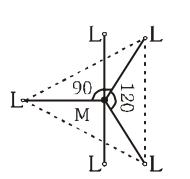
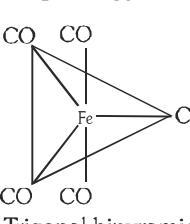
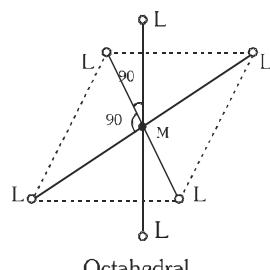
- CO is a strong ligand. So it is **low spin complex**.
- The empty one 4s and three 4p orbitals mix to form four new sp^3 hybridised orbitals.
- Each orbital accepts one electron pair from carbon monoxide molecule forming $[\text{Ni}(\text{CO})_4]$
- It is **diamagnetic** in nature, the shape of nickel tetra carbonyl is **tetrahedral** as shown above.



Note : In case, if metal belongs to 4d & 5d series all ligand will act as a strong field ligand.

e.g. $[\text{RhF}_6]^{3-}$, $[\text{Rh}(\text{NH}_3)_6]^{3-}$



Coordination Number	Hybridised orbital	Geometrical shape of the Complex	Examples of Complex
2	sp	 Linear	$[\text{Ag}(\text{NH}_3)_2]^+$ $[\text{Ag}(\text{CN})_2]^-$
3	sp ²	 Trigonal planar	$[\text{HgI}_3]^-$
4	sp ³	 Tetrahedral	$[\text{CuCl}_4]^{2-}$ $[\text{ZnCl}_4]^{2-}$ $[\text{FeCl}_4]^-$ $[\text{Ni}(\text{CO})_4]$ $[\text{Zn}(\text{NH}_3)_4]^{+2}$
4	dsp^2 $(\text{d}_{x^2-y^2} \text{ orbital})$	 Square planar	$[\text{PdCl}_4]^{2-}$ $[\text{Ni}(\text{CN})_4]^{2-}$ $[\text{Pt}(\text{NH}_3)_4]^{+2}$ $[\text{Cu}(\text{NH}_3)_4]^{+2}$ $[\text{PtCl}_4]^{2-}$
5	sp ³ d	 Trigonal bipyramidal	$[\text{CuCl}_5]^{3-}$
5	dsp ³	 Trigonal bipyramidal	$[\text{Fe}(\text{CO})_5]$
6	d^2sp^3 When d-orbitals are $(n-1)d$ -orbitals (Inner orbital complexes) or sp^3d^2 When d-orbitals are nd orbitals (Outer orbital complexes) In both cases d-orbitals are d_{z^2} and $\text{d}_{x^2-y^2}$ orbitals	 Octahedral	$[\text{Cr}(\text{NH}_3)_6]^{+3}$ $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$ $[\text{Fe}(\text{CN})_6]^{-3}$ $[\text{Co}(\text{NH}_3)_6]^{+3}$ $[\text{PtCl}_6]^{2-}, [\text{CoF}_6]^{-3}$



BEGINNER'S BOX-3

1. Complex ion square planar geometry :-

(1) $[\text{Ni}(\text{CN})_4]^{2-}$	(2) $[\text{Cu}(\text{CN})_4]^{-2}$	(3) $[\text{Cu}(\text{NH}_3)_4]^{+2}$	(4) All
-------------------------------------	-------------------------------------	---------------------------------------	---------
2. Which is low spin complex ?
 (1) $[\text{Fe}(\text{CN})_6]^{3-}$ (2) $[\text{Co}(\text{NO}_2)_6]^{3-}$ (3) $[\text{Mn}(\text{CN})_6]^{3-}$ (4) All
3. For the complex $[\text{Fe}(\text{CO})_x]$ what is wrong :-

(1) It is σ - π bonded organometallic compound	(2) In the complex value of $x = 6$
(3) In the complex CO is π -acid ligand	(4) It is trigonal bipyramidal shape
4. In the complex ion ML_6^{n+} , M^{n+} has five d-electrons and L is weak field ligand. According to crystal field theory, the magnetic properties of the complex ion corresponds to how many unpaired electrons
 (1) 0 (2) 5 (3) 2 (4) 3
5. Among $[\text{Ni}(\text{CO})_4]$, $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{Cl})_4]^{2-}$:
 (1) $[\text{Ni}(\text{CO})_4]$ and $[\text{Ni}(\text{Cl})_4]^{2-}$ are diamagnetic and $[\text{Ni}(\text{CN})_4]^{2-}$ is paramagnetic
 (2) $[\text{Ni}(\text{Cl})_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic and $[\text{Ni}(\text{CO})_4]$ is paramagnetic
 (3) $[\text{Ni}(\text{CO})_4]$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic and $[\text{Ni}(\text{Cl})_4]^{2-}$ is paramagnetic
 (4) $[\text{Ni}(\text{CO})_4]$ is diamagnetic and $[\text{Ni}(\text{Cl})_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are paramagnetic
6. Which is correct geometry in the case of $[\text{NiCl}_4]^{2-}$ complex ?
 (1) Tetrahedral (2) Octahedral (3) Square planar (4) Pyramidal
7. For $\text{K}_3[\text{CoF}_6]$, incorrect statement is :
 (1) It is high spin complex (2) Its magnetic moment is $\sqrt{24}$ BM
 (3) Primary valency of Co is six (4) Hybridisation state of CoF_6^{3-} is sp^3d^2
8. Which of the following compound is square planar and does not have any unpaired electron:
 (a) $[\text{Cu}(\text{NH}_3)_4]^{+2}$ (b) XeF_4 (c) $[\text{Ni}(\text{CO})_4]$ (d) $[\text{NiCl}_4]^{-2}$ (e) $[\text{Ni}(\text{CN})_4]^{-2}$ (f) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 (1) a, e, f (2) a, b, c (3) b, e (4) b, c, f
9. Which of the following complex does not have chelation
 (1) $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$ (2) $[\text{Pt}(\text{en})_2]\text{Cl}_2$ (3) $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ (4) $\text{K}_2[\text{Ni}(\text{EDTA})]$
10. Match list - I with list - II and choose the correct answer from the code given below

List - I (complex) List - II (geometry)

(A) $[\text{Ni}(\text{CN})_4]^{-2}$	(a) Octahedral
(B) $[\text{Pt}(\text{NH}_3)_6]^{+4}$	(b) Squareplanar
(C) $[\text{Ag}(\text{NH}_3)_2]^+$	(c) Tetrahedral
(D) $[\text{Zn}(\text{NH}_3)_4]^{+2}$	(d) Linear

A	B	C	D
(1) b	a	d	c
(2) a	b	c	d
(3) c	d	b	a
(4) b	c	d	a



(C) Crystal field theory

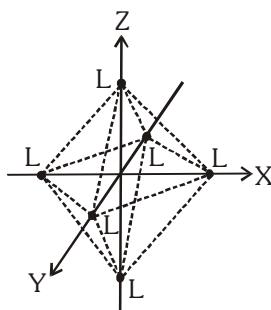
Crystal Field Theory : This is a model of electronic structure of transition-metal complexes that considers how the energies of the d-orbitals of a metal ion are affected by the electric field of the ligand. According to this theory.

- The ligands in a transition-metal complex are treated as point charges.
- A ligand anion becomes simply a point of negative charge. A neutral molecule, with its electron pair that it donates to the metal atom, is replaced by a negative charge, representing the negative end of the molecular dipole.
- In the electric field of these negative charges, the five d orbitals of the metal atom no longer have exactly same energy. Splitting of five degenerate d-orbitals of the metal ion into sets of orbitals having different energies is called crystal field splitting.
- The extent of splitting of metal d-orbitals depends upon the nature and number of ligands surrounding it and the charge on the central metal ion.
- The extent of splitting of metal d-orbitals determines the magnetic and spectroscopic properties of the complexes.

SPLITTING IN OCTAHEDRAL COMPLEXES

In an octahedral complex, the co-ordination number is 6. The metal ion is at the centre and the ligands occupy the six corners of the octahedron as shown in figure.

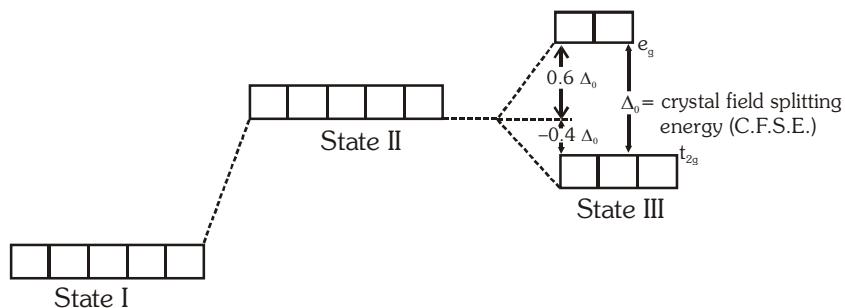
We know that two orbitals, $d_{x^2-y^2}$ and d_{z^2} are oriented along the axis while the remaining three orbitals, viz., d_{xy} , d_{yz} and d_{zx} are oriented in between the axis.



The two orbitals $d_{x^2-y^2}$ and d_{z^2} are designated as e_g orbitals while the three orbitals d_{xy} , d_{yz} and d_{zx} are designated as t_{2g} orbitals. As the six ligands approach the central ion along the axis, e_g orbitals, are repelled more by the ligand than in the t_{2g} orbitals.

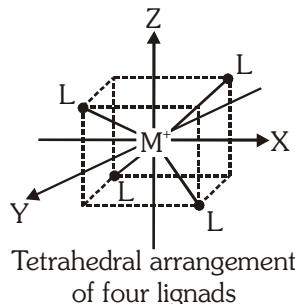
In other words, the energy of the d_{z^2} and $d_{x^2-y^2}$ orbitals increases much more than the energy of the d_{xy} , d_{yz} and d_{zx} orbitals.

Thus, in octahedral complexes, the five d-orbitals split up into two sets : one set consisting of two orbitals ($d_{x^2-y^2}$ and d_{z^2}) of higher energy (e_g orbitals) and the other set consisting of three orbitals (d_{xy} , d_{yz} and d_{zx}) of lower energy (t_{2g} orbitals).



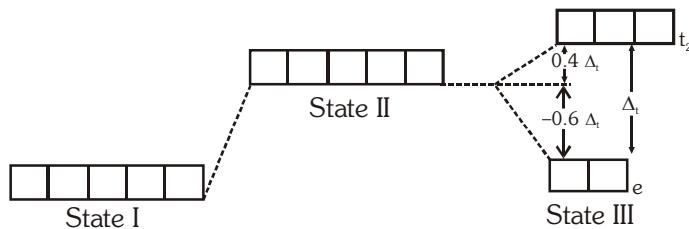
Splitting in tetrahedral complex

The co-ordination number for tetrahedral complexes is 4. The tetrahedral arrangement of four ligands surrounding a metal ion may be visualized by placing ligands at the alternate corners of a cube, as shown in figure.



It can be shown that in a tetrahedral structure, none of the d-orbitals points exactly towards the ligands. When ligand approaches it is more close d_{xy} , d_{yz} , d_{zx} in comparision of $d_{x^2-y^2}$ and d_{z^2} because d_{xy} , d_{yz} , d_{zx} are between the axis and d_{z^2} and $d_{x^2-y^2}$ are along the. So d_{xy} , d_{yz} , d_{zx} feels more repulsion as compare to d_{z^2} and $d_{x^2-y^2}$.

Thus, the d orbitals are also splitted into two groups but in a reverse order. The three orbitals, d_{xy} , d_{yz} and d_{zx} , designated as t_2 orbitals, now have higher energy than the two orbitals $d_{x^2-y^2}$ and d_{z^2} designated as eg-orbitals.



Calculation of crystal field stabilizing energy (CFSE)

$$(i) \text{ For octahedral CFSE} = [-0.4(n_{t_{2g}}) + 0.6(n_{eg})]\Delta_0 + \text{Pairing energy (P.E.)}$$

where $n_{t_{2g}}$ = number of electron in t_{2g} orbitals

n_{eg} = number of electron in eg orbitals

Δ_0 = crystal field **splitting** energy

$$(ii) \text{ For tetrahedral CFSE} = [-0.6(n_e) + 0.4(n_{t_2})]\Delta_t + \text{Pairing energy (P.E.)}$$

where n_{t_2} = number of electron in t_2 orbitals

n_e = number of electron in e orbitals

Δ_t = crystal field **splitting** energy

Example

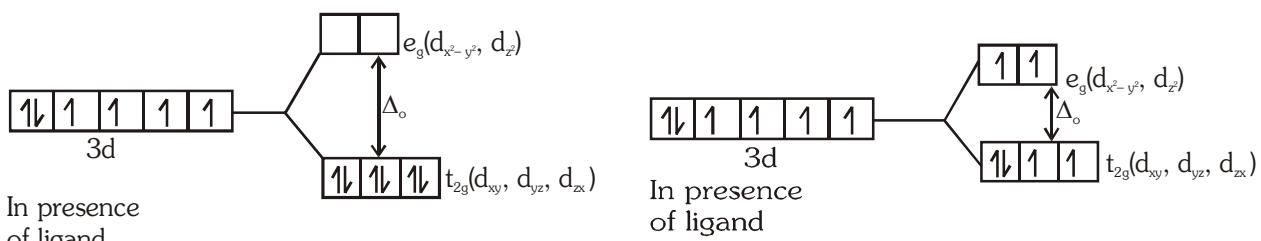
Explain the formation of $\text{Na}_4[\text{Fe}(\text{CN})_6]$ and $\text{Na}_4[\text{FeF}_6]$? Show which is low spin and which is high spin complex and also calculate the Crystal field stabilisation energy (CFSE) ?

Solution

In given compounds CN^- is strong field ligands and F^- is weak field ligand and in both compounds ions is in +2 oxidation state d^6 configuration.

So in $\text{Na}_4[\text{Fe}(\text{CN})_6]$

$\text{Na}_4[\text{FeF}_6]$



For octahedral CFSE = $[-0.4(n_{t_{2g}}) + 0.6(n_{e_g})]\Delta_0 + \text{P.E.}$

where $n_{t_{2g}}$ = number of electron in t_{2g} orbitals

n_{e_g} = number of electron in e_g orbitals

$\text{Na}_4[\text{Fe}(\text{CN})_6]$ CFSE = $-2.4 \Delta_0 + 3P$ [$n_{t_{2g}} = 6, n_{e_g} = 0$]

$\text{Na}_4[\text{Fe}(\text{F})_6]$ CFSE = $-0.4 \Delta_0 + P$ [$n_{t_{2g}} = 4, n_{e_g} = 2$]

where P = pairing energy to pair up electron.

Factors affecting Δ

factor affecting splitting

(i) Strength of ligand [C.F.S.E. is more in case of S.F.L. as compared to W.F.L.]

(ii) Oxidation state of central metal ion [C.F.S.E. \propto oxidation state]

(iii) Transition series (d-series) [C.F.S.E. , 5d > 4d > 3d]

(iv) Geometry (number of ligands). [$\Delta_{sq} > \Delta_0 > \Delta_t$]

$$\Delta_{sp} = \frac{4}{3} \Delta_0 \quad ; \quad \Delta_t = \frac{4}{9} \Delta_0 ; \quad [\Delta_{sp} = 1.3 \Delta_0]$$

Factors affecting strength of ligands

Strength of ligand depends upon :

(i) good σ donor (ii) good π acceptor (iii) high negative charge (iv) Small in size

Spectro-chemical series for ligands

Series which shows the relative strength of ligands

I^- (weakest) < Br^- < SCN^- < Cl^- < S^{2-} > NO_3^- < F^- < OH^- < $\text{C}_2\text{O}_4^{2-}$ < H_2O < NCS^- < edta^{4-} < NH_3 < en < NO_2^- < CN^- < CO (strongest)

APPLICATION OF CRYSTAL FIELD THEORY

Applications of C.F.T are

- (i) To predict the geometry that the compound is either inner orbital or outer orbital complex.
- (ii) To calculate the magnitude of paramagnetism.
- (iii) To show the colour property.

Que.

Give the magnetism in following configuration

(i) d^4 high spin octahedral	(ii) d^4 low spin octahedral
(iii) d^5 high spin octahedral	(iv) d^5 tetrahedral
(v) d^6 tetrahedral	(vi) d^8 low spin octahedral
(vii) d^7 tetrahedral	(viii) d^7 high spin octahedral.

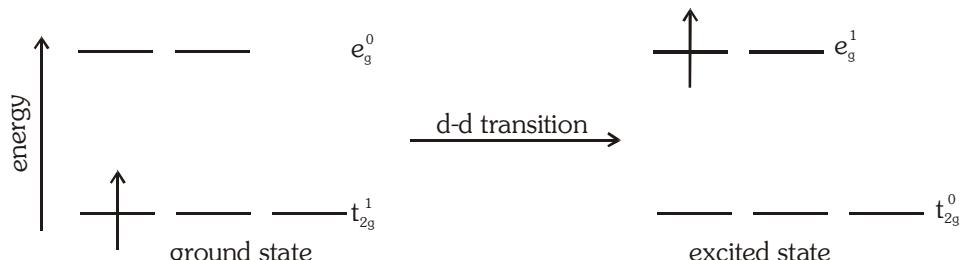
Solution

(i) four unpaired electron	(ii) two unpaired electron
(iii) five unpaired electron	(iv) five unpaired electron
(v) four unpaired electron	(vi) two unpaired electron
(vii) three unpaired electron	(viii) three unpaired electron

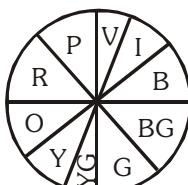
(II)

COLOUR PROPERTY :

Reason for colour in complexes is due to d-d-transition



Complementary colour wheel



For example complementary colour of red is blue green.



Example. $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is violet in colour explain using CFT.

Solution In $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ d-orbitals of Ti^{3+} lost their degeneracy in the presence of octahedral ligand field and produce t_{2g^1} & eg^0 . orbital of different energy complex absorbed visible light for excitation of electron from t_{2g^0} to eg^1 (d-d transition) and show complimentary violet colour.

Example. How the complex compounds show the colour?

Solution When d-electrons absorb energy from visible region they will get excited. Absorbed energy is related to a particular wavelength.

$$E(\Delta)_{\text{absorbed}} = \frac{hc}{\lambda_{\text{absorbed}}}$$

when electrons fall into lower energy level it will show colour whose wavelength (λ) is the complimentary of absorbed wavelength ($\lambda_{\text{absorbed}}$).

Example. Why violet coloured $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$ becomes colourless when heated ?

Solution When $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$ is heated water molecules are removed and in the absence of ligand crystal field splitting does not occur and hence the substance is colourless.

Example. $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ are of different colours in dilute solutions. Why ?

Solution It is due to difference in power of ligands.

Example. What will be the correct order for the wavelengths of absorption in the visible region for the following : $[\text{Ni}(\text{NO}_2)_6]^{4-}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$?

Solution $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} > [\text{Ni}(\text{NH}_3)_6]^{2+} > [\text{Ni}(\text{NO}_2)_6]^{4-}$

GOLDEN KEY POINTS

- Red colour of ruby is due to presence of small amount of Cr^{3+} in atmosphere of Al_2O_3
- Green colour of emerald is due to presence of Cr^{3+} in atmosphere of $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ [beryl]
- Complex become colourless in absence of ligand field because in absence of ligand d-d-transition does not occur.
- $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ become colourless on heating due to removal of water molecules.
- Anhydrous CuSO_4 is colourless but hydrated CuSO_4 is blue due to moisture.
- Halogens are coloured due to the HOMO-LUMO transition.
- KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, CrO_2Cl_2 are coloured due to charge transfer spectra.



3.4 STABILITY OF CO-ORDINATION COMPOUNDS IN SOLUTION

According to thermodynamic stability, the reaction between a metal ion and the ligands may be considered as a Lewis acid base reaction in solution. If the equilibrium constant is high then the complex obtained is thermodynamically stable in solution. The reaction can be written as follows : $M + nL \rightleftharpoons [ML_n]$

The stability constant K , of the complex $[ML_n]$ is given by the relation, $K = \frac{[ML_n]}{[M][L]^n}$. The greater the value of K , more stable is the complex.

The strength of a complex ion also depends upon —

- (i) Higher charge of the central metal ion.
- (ii) Greater base strength of the ligand.
- (iii) Ring formation (chelation) in structure of complexes.

BEGINNER'S BOX-4

Complexes

Properties

Complexes	Property
(i) $(CoCl_6)^{3-}$	(a) No. of electrons in t_{2g} = 5
(ii) $[Co(OX)_3]^{3-}$	(b) No. of electrons in e_g = 0
(iii) $[Co(H_2O)_6]^{2+}$	(c) No. of electrons in t_{2g} = 6
(iv) $[Fe(CN)_6]^{4-}$	(d) No. of electrons in e_g = 2

[Ans. i-d, ii-b, iii-a,d iv-c]

7. Which order is correct

(1) $[\text{NiCl}_6]^{4-} > [\text{NiCl}_4]^{2-}$
 (2) $[\text{Cr}(\text{en})_3]\text{Cl}_3 > [\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
 (3) $[\text{Co}(\text{CN})_6]^{4-} > [\text{Co}(\text{CN})_6]^{3-}$
 (4) All of these

splitting energy Δ_0
crystal field stabilisation energy
reducing behaviour

8 Which is inner d-complex

(1) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ (2) $[\text{RhF}_6]^{3-}$

(3) $[\text{IrF}_6]^{3-}$ (4) AlI_3

9 Which stability order is incorrect

(1) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-} > [\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

(3) $[\text{Ni}(\text{en})]^2+ > [\text{Ni}(\text{dmg})]$

$$(2) [Fe(EDTA)]^{2-} > [Fe(en)]^{3+}$$

$$(4) [Fe(CN)]^{3-} > [Fe(CN)]^{4-}$$

10 The complex exhibit lowest energy absorption band is

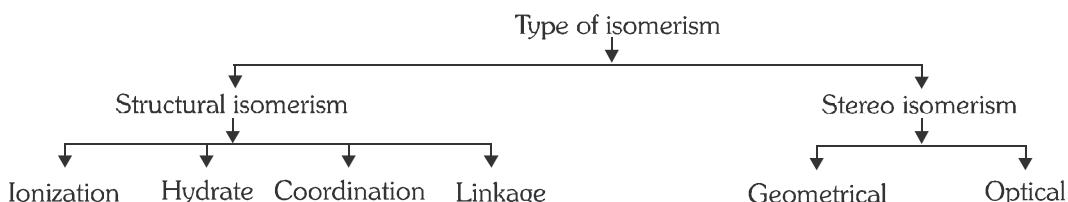
(1) $[\text{NiCl}_4]^{2-}$ (2) $[\text{Ni}(\text{CO})_4]$

(3) $[\text{Ni}(\text{CN})_4]^{2-}$

(4) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$

3.5 ISOMERISM IN COMPLEXES

- (a) Compounds which have the same molecular formula, but differ in their properties due to the difference in structure are called as **Isomers**.
- (b) Isomerism is commonly considered, to be the characteristic of only organic compounds, it is also found although less frequently among inorganic substances.
- (c) **Classification of isomerism :**



- **Structural Isomerism**

It arises due to the difference in the type of chemical linkages and distribution of ligands within and outside the coordination sphere.

- **Ionisation Isomers**

The type of isomerism which is due to the exchange of groups or ion between the coordinating sphere and the ionisation sphere.

Ex. (a) $\text{Co}(\text{NH}_3)_4 \text{Br}_2 \text{SO}_4$ can represent

- (i) $[\text{Co}(\text{NH}_3)_4 \text{Br}_2] \text{SO}_4$ (red violet)
- (ii) $[\text{Co}(\text{NH}_3)_4 \text{SO}_4] \text{Br}_2$ (red).

These complexes give sulphate ion and bromide ion respectively

(b) $[\text{Pt}(\text{NH}_3)_4 \text{Cl}_2] \text{Br}_2$ and $[\text{Pt}(\text{NH}_3)_4 \text{Br}_2] \text{Cl}_2$

(c) $[\text{Co}(\text{NH}_3)_4 (\text{NO}_3)_2] \text{SO}_4$ and $[\text{Co}(\text{NH}_3)_4 \text{SO}_4] (\text{NO}_3)_2$

- **Hydrate Isomers**

This type of isomerism is due to presence of different number of water molecules inside a coordination sphere.

Ex. (a) $\text{Cr}(\text{H}_2\text{O})_6 \text{Cl}_3$ has three possible structures

- (i) $[\text{Cr}(\text{H}_2\text{O})_6] \text{Cl}_3$ violet
- (ii) $[\text{Cr}(\text{H}_2\text{O})_5 \text{Cl}] \text{Cl}_2 \cdot \text{H}_2\text{O}$ green
- (iii) $[\text{Cr}(\text{H}_2\text{O})_4 \text{Cl}_2] \text{Cl} \cdot 2\text{H}_2\text{O}$ dark green.

These complexes differ from one another with respect to the number of water molecules acting as ligands.

Other hydrate isomers are

(i) $[\text{Co}(\text{NH}_3)_4 \text{H}_2\text{O} \text{Cl}] \text{Cl}_2$

(ii) $[\text{Co}(\text{NH}_3)_4 \text{Cl}_2] \text{Cl} \cdot \text{H}_2\text{O}$

- **Linkage or Salt Isomers**

- (a) This type of isomerism arises due to presence of ambidentate ligands like NO_2^- , CN^- and SCN^-
- (b) These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex.
- (c) Such type of isomers are distinguished by infra red (I.R.) spectroscopy.

Ex. (i) $[\text{Co}(\text{NH}_3)_5 \text{NO}_2] \text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5 \text{ONO}] \text{Cl}_2$

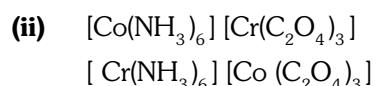
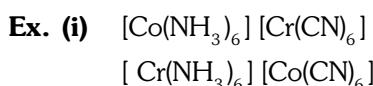
(ii) In NO_2^- ligand, The coordinating sites are nitrogen (i.e., NO_2^- Nitro ligand) or through oxygen (i.e. ONO Nitrito ligand)

(iii) The nitro isomer is yellow and is stable to acids whereas nitrito isomer is red and is decomposed by acids.



- **Coordination Isomers**

- This type of isomerism is exhibited when the complex has two complex ions in it - **Cationic and Anionic**.
- This type of isomerism is caused by the interchange of ligands between the two complex ions of the same complex.



- **Stereo Isomerism**

- They have same molecular formula, same constitution, they differ only with respect to the spatial orientation of ligands in space around the metal ion.
- The two stereo isomers which are possible are - Geometrical and optical.

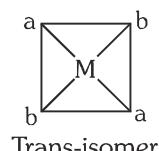
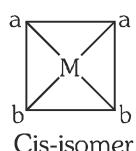
(A) Geometrical or cis - Trans Isomers

- The ligands occupy different positions around the central metal ion.
- When two identical ligands are coordinated to the metal ion from same side then it is **cis isomer**. (Latin, cis means same).
- If the two identical ligands are coordinated to the metal ion from opposite side then it is **Trans isomer** (in Latin, Trans means across).
- These geometrical isomers differ in physical as well as in chemical properties.
- Geometrical isomerism is most important in compounds with coordination numbers 4 and 6.
- 4-coordinated complexes with tetrahedral geometry do not exhibit cis- Trans isomerism, because relative position of ligands remain same for each other.
- It is exhibited by 4-coordinated complexes with square planar geometry.

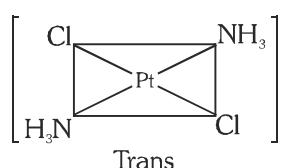
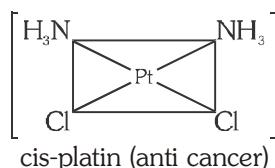
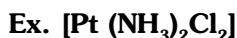
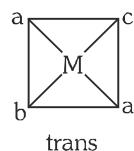
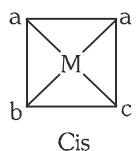
Note : There are only 5 possible cases which shows geometrical isomerism in square planar complex. such as Ma_2b_2 , Ma_2bc , Mabcd , M(AB)_2 , M(AB)cd

Geometrical Isomers With Coordination Number = 4 (Square Planar Complexes)

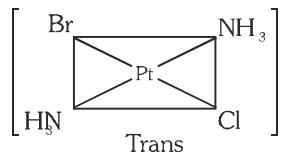
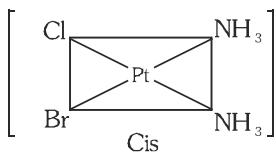
(i) Complexes with general formula, Ma_2b_2 (where both a and b are monodentate) can have Cis-and trans isomers.



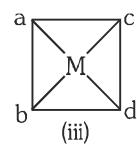
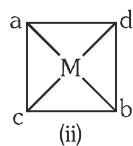
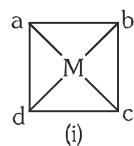
(ii) Complexes with general formula Ma_2bc can have Cis - and trans-isomers.



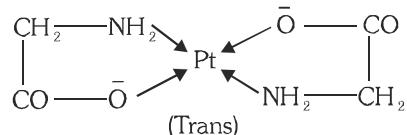
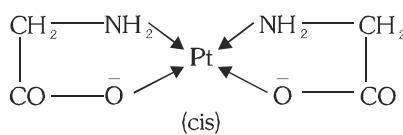
Ex. $[\text{Pt}(\text{NH}_3)_2\text{ClBr}]$



(iii) Complexes with general formula, **Mabcd** can have three isomers.

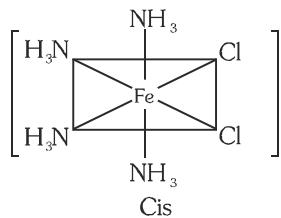
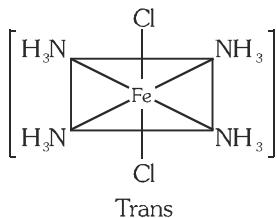


(iv) Diglycinato platinum (II) complexes

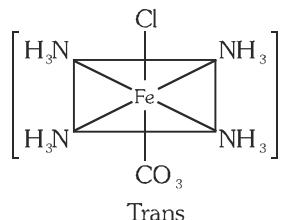
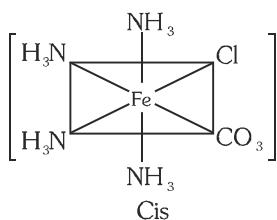


Geometrical isomers with Coordination number = 6

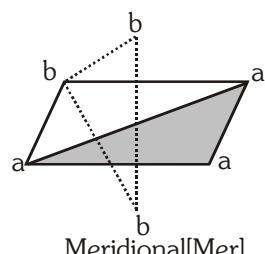
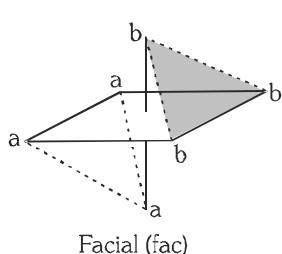
(i) $[\text{Fe}(\text{NH}_3)_4\text{Cl}_2]$



(ii) $[\text{Fe}(\text{NH}_3)_4\text{ClCO}_3]$



(iii) Facial and Meridional isomerism (Ma, b_2)



Note : Other 6-Coordinated geometrical isomers are –

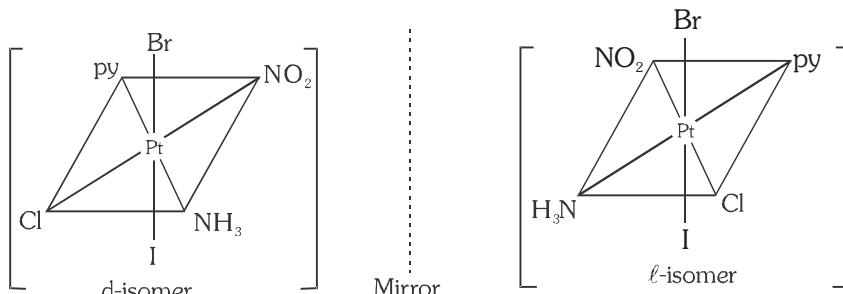
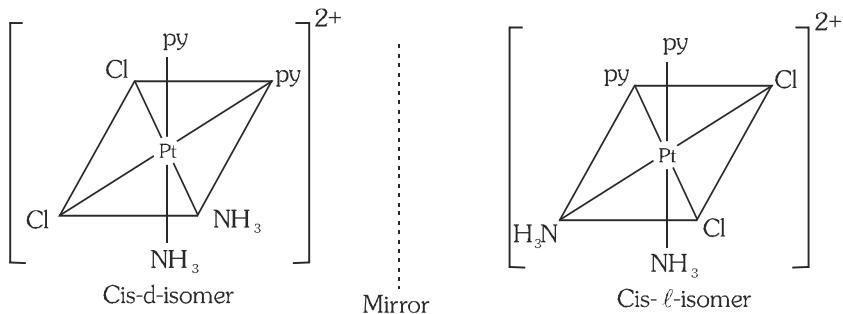
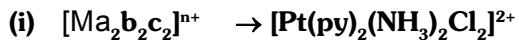
General formula	Total No. of geometrical isomers
Mabcdef	15 (30 optical isomers)
Ma ₂ bcde	9
Ma ₂ b ₂ cd	6
Ma ₂ b ₂ c ₂	5
Ma ₃ bcd	4
Ma ₃ b ₂ c	3
Ma ₃ b ₃	2
Ma ₄ bc	2
Ma ₄ b ₂	2
Ma ₅ b	Nil
Ma ₆	Nil

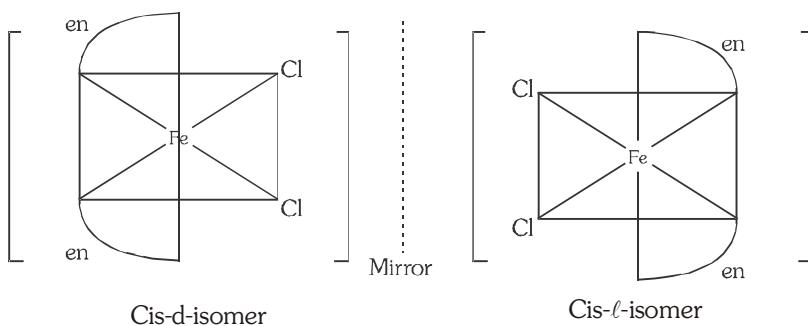
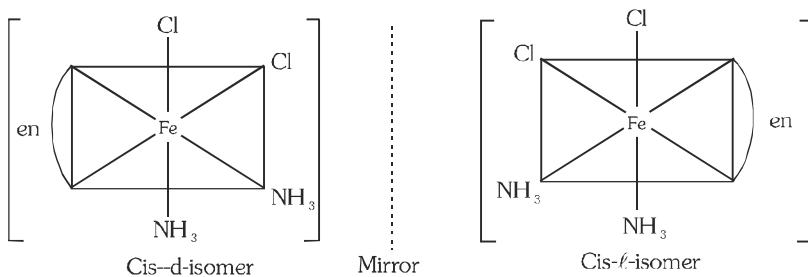
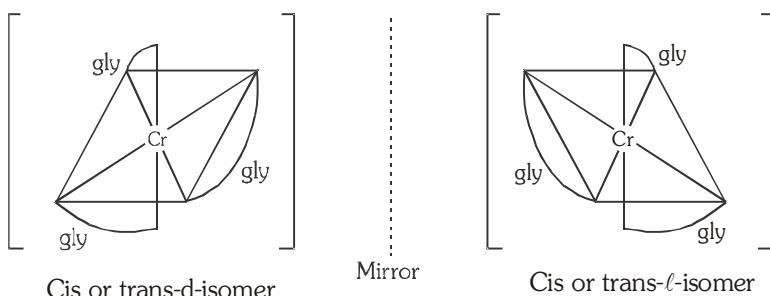
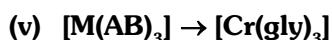
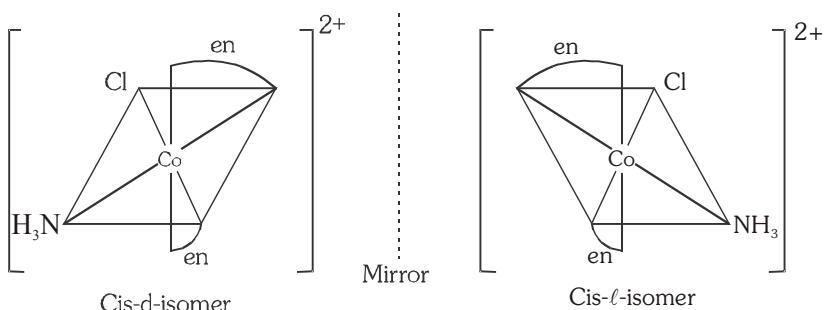
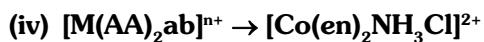
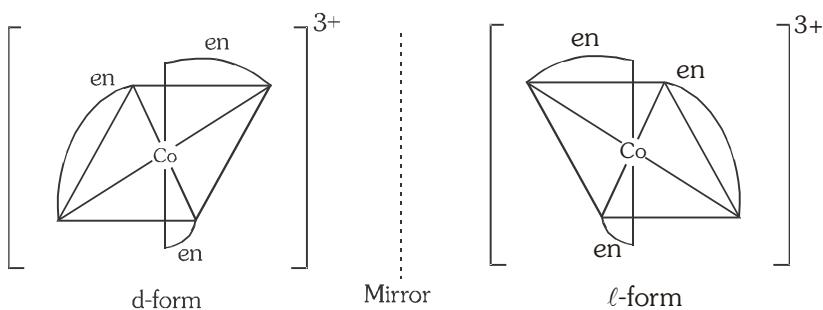
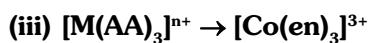
Here M = central atom ; a, b, c, d, e, f = Monodentate ligands

(B) Optical Isomers

- Optically active complexes are those which are non-superimposable over the mirror image structure.
- An optically active complex is one which is asymmetric in nature i.e., not divisible into two identical halves.
- The complex which rotates plane polarised light to left hand side is **laevo rotatory** i.e. '*l*' or '*—*' and if the complex rotates the plane polarised light to right hand side then it is **dextro rotatory** '*d*' or '*+*'.
- Thus complexes which have same physical and chemical properties but differ in their action towards plane polarised light are called as **optical isomers**.
- The '*d*' and '*l*' isomers of a compound are called as **Enantiomers or Enantiomorphs**.

Optical isomers with Coordination number = 6





BEGINNER'S BOX-5

1. Which of the following sets is/are example of co-ordination isomerism in complexes ?
 - (1) $[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{CN})_6]$ and $[\text{Co}(\text{CN})_6] [\text{Cr}(\text{NH}_3)_6]$
 - (2) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$
 - (3) $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Cr}(\text{NH}_3)_5]\text{SO}_4\text{Br}$
 - (4) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and $[\text{Pt}(\text{NH}_3)_4] [\text{PtCl}_4]$
2. Which of the following does/do not exhibit optical isomerism

(1) Tetrahedral complexes	(2) Square planar complexes
(3) Octahedral complexes	(4) Polynuclear complexes
3. The number of geometrical isomers of $[\text{Co}(\text{NH}_3)_3(\text{NO}_3)_3]$ are :

(1) 0	(2) 2	(3) 3	(4) 4
-------	-------	-------	-------
4. Which of the following coordination entity form racemic mixture when mixed in equimolar concentration

(1) $[\text{Cr}(\text{OX})_3]^{3-}$	(2) $[\text{Co}(\text{en})_2\text{Cl}_2]^{1+}$	(3) $[\text{Co}(\text{en})\text{Cl}_4]^-$	(4) All
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5. The number of isomeric forms in which $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{1+}$ ion can occur is

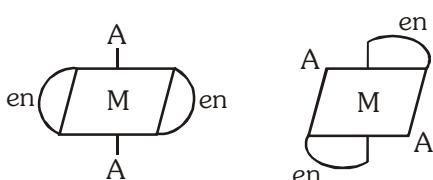
(1) 2	(2) 3	(3) 4	(4) 1
-------	-------	-------	-------
6. The total number of possible isomer for the complex comp. :- $[\text{Cu}(\text{NH}_3)_4] [\text{PtCl}_4]$

(1) 3	(2) 6	(3) 5	(4) 4
-------	-------	-------	-------
7. The complexes $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_5]\text{Cl}_2$ and $[\text{Co}(\text{ONO})_2(\text{NH}_3)_5]\text{Cl}_2$ are the examples of

(1) Coordination isomerism	(2) Ionisation isomerism
(3) Geometrical isomerism	(4) Linkage isomerism
8. The type of isomerism exhibited $[\text{Rh}(\text{en})_2\text{Cl}_2][\text{Rh}(\text{en})\text{Cl}_4]$ and $[\text{Rh}(\text{en})_3][\text{RhCl}_6]$ is

(1) Linkage	(2) Coordination
(3) Ligand	(4) Ionisation
9. Which of the following will give maximum number of isomers :-

(1) $[\text{Co}(\text{py})_3(\text{NH}_3)_3]^{3+}$	(2) $[\text{Ni}(\text{en})(\text{NH}_3)_4]^{2+}$
(3) $[\text{Fe}(\text{C}_2\text{O}_4)_2(\text{en})_2]^{2-}$	(4) $[\text{Cr}(\text{NO}_2)_2(\text{NH}_3)_4]^+$
10. The Complexes given below are :-



- (1) Geometrical isomers (2) Position isomers (3) Optical isomers (4) Identical



3.6 ORGANOMETALLIC COMPOUNDS

Compounds in which C-atom is directly bonded with less electronegative element.

(Ge, Sb, B, Si, P, As) Also form organometallic compounds.

Ex. $\begin{cases} R - Zn - R & \text{dialkyl zinc (Frankland reagent)} \\ R - Mg - X & \text{Alkyl Magnesium halide (Grignards reagent)} \end{cases}$

(b) Sodium acetate $\text{CH}_3 - \overset{\text{O}}{\underset{\text{||}}{\text{C}}} - \text{O} - \text{Na}$ These are not organometallic compounds because in these compounds metal is not directly attached with carbon atom.
 Sodium ethoxide $\text{C}_2\text{H}_5 - \text{O} - \text{Na}$
 Sodium Mercaptide $\text{H}_3\text{C} - \text{SNa}$

(c) $\text{B}(\text{OCH}_3)_3$ is not OMC \rightarrow $\begin{array}{c} \text{H}_3\text{CO} \\ | \\ \text{B} - \text{OCH}_3 \\ | \\ \text{H}_3\text{CO} \end{array}$ and $\text{CH}_3\text{B}(\text{OCH}_3)_2$ is OMC \rightarrow $\begin{array}{c} \text{OCH}_3 \\ | \\ \text{CH}_3 - \text{B} - \text{OCH}_3 \\ | \\ \text{OCH}_3 \end{array}$

(d) Carbides and carbonates are not considered OMC because in these compounds metal carbon bond has ionic nature.

Classification of Organometallic Compounds

OMC can be classified into three main categories –

σ - bonded OMC : These compounds are formed mostly by non transition and metalloid elements.

Ex. $R - Mg - X$ (Grignard's reagent)

$(\text{CH}_3)_2\text{Zn}$ (Dimethyl zinc or Frankland's reagent)

$R_2\text{Cd}$ (dialkyl cadmium)

$(\text{C}_2\text{H}_5)_4\text{Pb}$ (Tetra ethyl lead) – used as antiknocking agent in petrol.

$(\text{C}_2\text{H}_5)_3\text{Al} + \text{TiCl}_4$ (Ziegler natta catalyst) – Heterogeneous catalyst, used in polymerisation of alkene.

π - bonded OMC : These are usually formed by transition metals.

Ex. Ferrocene $[\text{Fe}(\eta^5 - \text{C}_5\text{H}_5)_2]$ where η = No. of carbon atoms combined with metal atom.

Zeise's salt $\text{K}[\text{PtCl}_3(\eta^2 - \text{C}_2\text{H}_4)]$

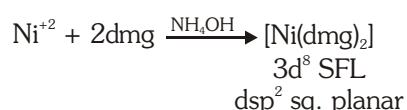
Dibenzene chromium $[\text{Cr}(\eta^6 - \text{C}_6\text{H}_6)_2]$

σ and π - bonded OMC : Transition metals of gp. 6, 7, 8, 9 and 10 in their zero oxidation state form such type of OMC. The carbonyl compounds of these metals have both σ and π bonds.

Ex. $[\text{Ni}(\text{CO})_4], [\text{Fe}(\text{CO})_5], [\text{Mn}_2(\text{CO})_{10}]$
 $[\text{M}(\text{CO})_6]$ [M = Cr, Mo, W]

3.7 APPLICATION OF COORDINATION CHEMISTRY

(a) Test of Ni^{+2} : Ni^{+2} ion give rosy red ppt when react with dmgo in weak alkaline medium.

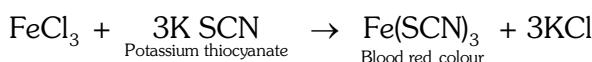


(b) Test of S^{2-} : $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})] \rightarrow \text{Na}_4[\text{Fe}(\text{CN})_5(\text{NOS})]$
 sodium nitro prousside violet colour

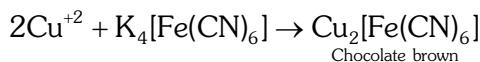
(c) Test of Fe^{+2} & Fe^{+3} :



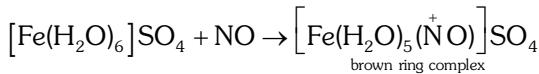
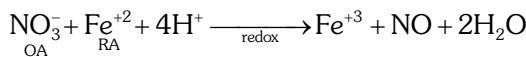
(d) Test of Fe^{+3}



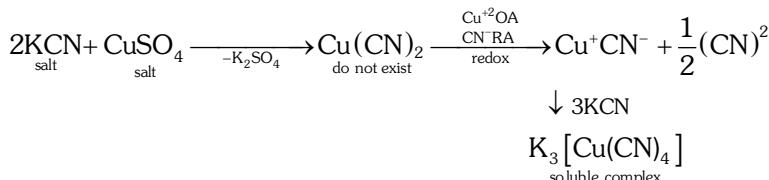
(e) Test of Cu⁺2



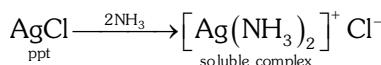
(f) Brown ring test : Test for Nitrate ion



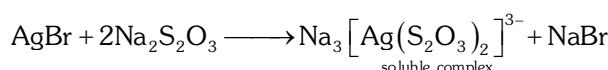
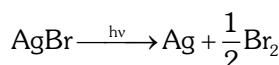
(g) If excess of KCN & KI is added in CuSO₄ insoluble CuCN & Cul is formed which later turn into soluble complex.



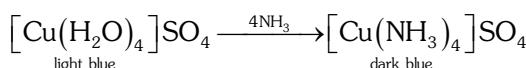
(h) AgCl or AgBr ppt (Not AgI) are soluble in ammonia & NH₄OH



(i) In photography : undecomposed AgBr is removed from photography film by using hyposolution [Na₂S₂O₃.5H₂O]



(j) Light blue colour of aqueous solution of CuSO₄ turn into dark blue in presence of ammonia



But in the presence of acid in above there is no colour change



- (k)** Rusting spots of iron [Fe₂O₃.XH₂O] can be removed by using oxalic acid.
- (l)** cyano complex are used for electroplating of Ag or Au due to high stability.
e.g. [Ag(CN)₂]⁻
- (m)** **Wilkinson catalyst** [RhCl(PPh₃)₃] is used for hydrogenation of alkene. (Homogeneous catalysis)
- (n)** [EDTA]⁴⁻ is used for **estimation of hardness of water**.
- (o)** [Ca(EDTA)]²⁻ is **used to remove Pb poison**.
[Ca(EDTA)]²⁻ + Pb²⁺ → [Pb(EDTA)]²⁻ + Ca²⁺

(p) Biological importance

Chlorophyll (Mg)	haemoglobin (Fe ⁺ 2)	Myoglobin (Fe ⁺ 2)
Vit B ₁₂ (Co)	Corboxypeptide (Zn)	Insulin (Zn)

JAHN TELLER EFFECT

In octahedral field if the d electrons are symmetrically arranged, they will repel all six ligands equally. Thus the structure will be a completely regular octahedron.

If the d electrons are unsymmetrically arranged, they will repel some ligands in the complex more than others. Thus the structure is distorted. The e_g orbitals point directly at the ligands. Thus unsymmetric filling of the e_g orbitals results in some ligands being repelled more than others. This causes a significant distortion of the octahedral shape. In contrast the t_{2g} orbitals do not point directly at the ligands, but point in between the ligand directions. Thus unsymmetric filling of the t_{2g} orbitals has only a very small effect on the stereochemistry. Distortion caused by unsymmetric filling of the t_{2g} orbitals is usually too small to measure.



If the d_{z^2} orbital contains one more electron than the $d_{x^2-y^2}$ orbital then the ligands approaching along $+z$ and $-z$ will face greater repulsion than the other four ligands. The repulsion and distortion result in elongation of the octahedron along the z -axis. This is called tetragonal distortion or tetragonal elongation.

If the $d_{x^2-y^2}$ orbital contains the extra electron, then elongation will occur along the x and y axes. This means that the ligands approach more closely along the z axis. Thus there will be four long bonds and two short bonds. This is equivalent to compressing the octahedron along the z axis, and is called tetragonal compression.

Example-I

Many Cu(+II) salts and complexes also show tetragonally distorted octahedral structures. Cu²⁺ has a d⁹ configuration:



To minimize repulsion with the ligands, two electron occupy the d_{z^2} orbital and one electron occupies $d_{x^2-y^2}$ orbital. Thus the two ligands along $+z$ and $-z$ are repelled more strongly than are the other four ligands.

Therefore according to Jahn Teller effect distortion in regular octahedral geometry occurs when unsymmetrical configuration is present in e_g orbitals of central metal ion/atom.

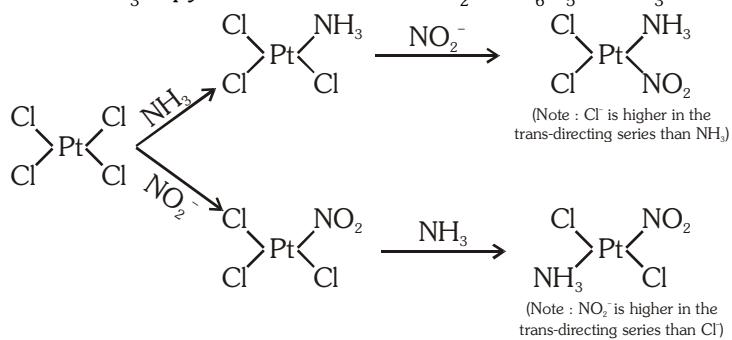
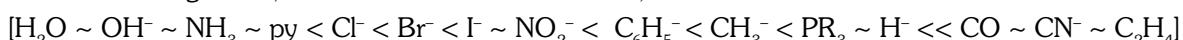
Example-II

High spin complexes in which J.T. effect is i.e. d¹, d², d³(negligible), d⁴, d⁶, d⁷, d⁹ observed.

TRANS EFFECT (The kinetic trans effect)

The kinetic trans effect, defined as the relationship between the rate of substitution of square planar complexes and the nature of the species trans to the ligands being displaced.

A trans-directing series, such as the one shown below, can be constructed :



In a substitution reaction in which there is more than one possibility as to which chloride will be replaced, the trans directing series is used to predict which structure will be possible.

BEGINNER'S BOX-6

1. $\text{K}_4[\text{Fe}(\text{CN})_6]$ reacts with FeCl_3 to form :-

(1) $\text{K}_3[\text{Fe}(\text{CN})_6]$	(2) $\text{K}_4[\text{Fe}(\text{CN})_3\text{Cl}_3]$	(3) $\text{K}_3[\text{Fe}(\text{CN})_5\text{Cl}]$	(4) $\text{KFe}[\text{Fe}(\text{CN})_6]$
--	---	---	--
2. A blue colouration is not obtained when :-

(1) NH_4OH is added to CuSO_4	(2) CuSO_4 solution reacts with $\text{K}_4[\text{Fe}(\text{CN})_6]$
(3) FeCl_3 reacts with $\text{K}_4[\text{Fe}(\text{CN})_6]$	(4) Anhydrous white CuSO_4 is dissolved in water
3. A reagent used for identifying nickel ion is :-

(1) Potassium ferrocyanide	(2) Phenolphthalein
(3) Dimethyl glyoxime	(4) EDTA
4. Match the following

Complex

- (A) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
- (B) $\text{K}_3[\text{Cu}(\text{CN})_4]$
- (C) $[\text{Ca}(\text{EDTA})]^{2-}$
- (D) $\text{K}_2[\text{Cd}(\text{CN})_4]$

(1) (A)-S,T, (B) T, (C) Q,R (D) P,T
 (3) (A)-P, (B) T, (C) Q,R (D) P,T

(P) reacts with H_2S gas
 (Q) estimation of hardness
 (R) removal of lead poisoning
 (S) anti cancer drug
 (T) coordination number of metal is = 4
 (2) (A)-S (B) T, (C) Q,R (D) P,T
 (4) (A)-R (B) T, (C) Q,R (D) P,T

Property

(P) reacts with H_2S gas
 (Q) estimation of hardness
 (R) removal of lead poisoning
 (S) anti cancer drug
 (T) coordination number of metal is = 4
 (2) (A)-S (B) T, (C) Q,R (D) P,T
 (4) (A)-R (B) T, (C) Q,R (D) P,T



5. A person suffering from lead poisoning should be fed with :-
(1) Hypo (2) Cis-platin (3) $[\text{Ca}(\text{EDTA})]^{2-}$ (4) DMG

6. Zeigler natta catalyst is :
(1) $[\text{RhCl}(\text{PPh}_3)_3]$ (2) $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{TiCl}_4$ (3) $\text{K}[\text{PtCl}_3(\eta^2 - \text{C}_2\text{H}_4)]$ (4) Pt/Rh

7. In which of the following process OMC is formed with the help of other OMC :
(1) $\text{SnCl}_4 + \text{Butyl lithium} \longrightarrow \text{Bu}_4\text{Sn} + 4\text{LiCl}$
(2) $\text{C}_2\text{H}_5\text{I} + 4\text{Pb/Na (alloy)} \longrightarrow (\text{C}_2\text{H}_5)_4\text{Pb} + 4\text{NaI} + 3\text{Pb}$
(3) $\text{Ni} + 4\text{CO} \longrightarrow [\text{Ni}(\text{CO})_4]$
(4) $\text{K}_2[\text{PtCl}_4] + \text{CH}_2 \longrightarrow \text{CH}_2 \longrightarrow \text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] + \text{KCl}$

8. Which is/are organometallic compound :-
(I) Grignard reagent (II) Sodium methoxide (III) trimethyl boron (IV) TEL
(1) Only I (2) I & II (3) I, II, IV (4) I, III, IV

9. Which of the following is an organometallic compound :
(1) $\text{Ti}(\text{OCOCH}_3)_4$ (2) $\text{Ti}(\text{OC}_6\text{H}_5)_4$ (3) $\text{Ti}(\text{OC}_2\text{H}_5)_3\text{C}_2\text{H}_5$ (4) $\text{Ti}(\text{OC}_2\text{H}_5)_4$

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	4	3	1			2	3	3	2
BEGINNER'S BOX-2	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	4	3	3	1	4	1	1	3	4
BEGINNER'S BOX-3	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	4	4	2	2	3	1	3	3	3	1
BEGINNER'S BOX-4	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	1	3	2	3		4	4	3	1
BEGINNER'S BOX-5	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	1	2	2	1,2	1	4	4	2	4	4
BEGINNER'S BOX-6	Que.	1	2	3	4	5	6	7	8	9	
	Ans.	4	2	3	1	3	2	1	4	3	



NCERT QUESTIONS (REASONING)

Q.1 Explain the term Degenerate orbitals :

Ans. Orbitals which have same energy in a subshell are known as degenerate orbitals.

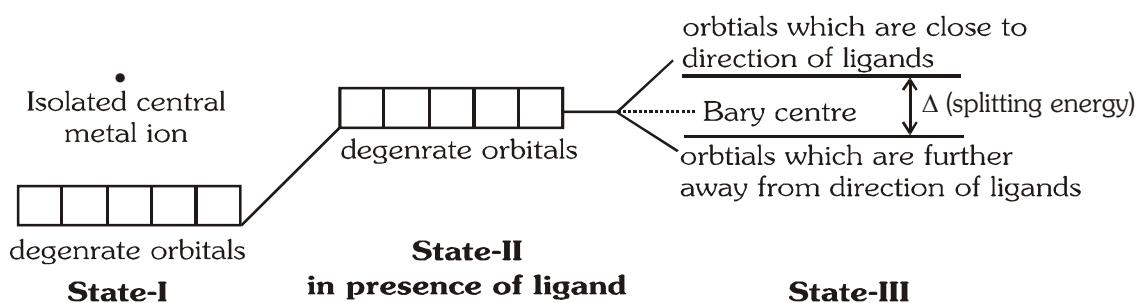
Q.2 What is crystal field splitting ?

Ans. According to CFT the interaction between a transition metal and ligands arises from the attraction between the positively charged metal cation and negative charge of ligand.

As a ligand approaches the metal ion, the electrons of ligand will be closer to some of the d-orbitals and farther away from other causing a loss of degeneracy.

The electrons in the d-orbitals and those in the ligand repel each other due to repulsion between like charges. Thus the d-electrons closer to the ligands will have a higher energy than those further away as a result in the d-orbitals splitting in energy.

This loss of degeneracy of d-orbital is known as crystal field splitting.



The state I represents degeneracy of all the five d-orbitals in the isolated central ion. The state II represents hypothetical degeneracy of all the orbitals at a higher energy level if the negative charge of all the ligands is assumed to be uniformly affecting the electrons in the d-orbitals of the metal ion. The state III represents crystal field splitting.

Q.3 Define (a) crystal field stabilisation energy (b) Pairing energy ?

Ans. (a) **Crystal field stabilisation energy** : The lowering in the energy of a transition metal ion in a given ligand environment due to crystal field effects.

(b) **Pairing energy** : The energy required to pair the electrons.

Q.4 Explain the term

(a) **Inner orbital complex and outer orbital complexes ?**

(b) **Low spin and high spin complexes ?**

Ans. (a) The empty 'd' orbitals involved in hybridisation may be inner (n-1)d or outer "nd" orbitals and these complexes are called as **Inner orbital complexes** and **outer orbital complexes** respectively.

For example in d^2sp^3 hybridisation (n-1)d, ns and np orbitals are mixed it forms inner orbital complex and in sp^3d^2 ns, np and nd orbitals are mixed so it forms outer orbitals complex.

(b) When the strong field ligand approaches to metal ion value to splitting energy (Δ) is greater than, pairing energy, so it is unfavourable to put electron into high energy orbitals. Therefore, the lower energy orbitals are completely filled before population of the upper sets starts according to the Aufbau principle. Such type of complexes are called low spin complex.

For low spin complexes

splitting energy (Δ) > pairing energy (P)

Weak field ligand causes a small splitting of the d-orbitals where splitting energy is less than pairing energy. It is easier to put electrons into the higher energy set of orbitals than to pair up in the same low energy orbitals because two electrons in the same orbitals repel each other. So one electron is put into each of the five d-orbitals before any pairing occurs in accordance with Hund rule.

Such complexes are known as high spin complex.

For high spin complexes splitting energy (Δ) < pairing energy (P)



Q.5 In octahedral complex if central metal have configuration d^1, d^2, d^3 always make inner orbital complex, Why ?

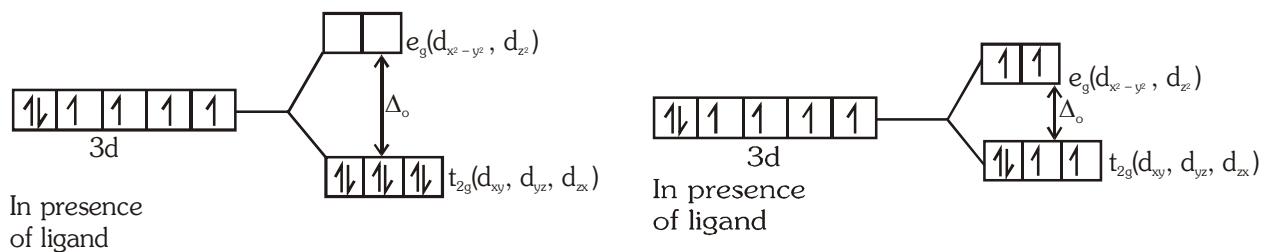
Ans. Central metal ion which have d^1, d^2, d^3 configuration have at least two vacant orbitals in any ligand environment or with any central metal ion with any oxidation state. So always make inner orbital complex.

Q.6 Explain the formation of $Na_4[Fe(CN)_6]$ and $Na_4[FeF_6]$? Show which is low spin and which is high spin complex and also calculate the Crystal field stabilisation energy (CFSE) ?

Ans. In given compounds CN^- is strong field ligand and F^- is weak field ligand and in both compounds ions is in +2 oxidation state d^6 configuration.

So in $Na_4[Fe(CN)_6]$

$Na_4[FeF_6]$



$$\text{For octahedral CFSE} = \left[-0.4(n_{t_{2g}}) + 0.6(n_{e_g}) \right] \Delta_o + nP$$

where $n_{t_{2g}}$ = number of electron in t_{2g} orbitals

n_{e_g} = number of electron in e_g orbitals

$$Na_4[Fe(CN)_6] \text{ CFSE} = -2.4 \Delta_o + 3P \quad [n_{t_{2g}} = 6, n_{e_g} = 0]$$

$$Na_4[Fe(F)_6] \text{ CFSE} = -0.4 \Delta_o + P \quad [n_{t_{2g}} = 4, n_{e_g} = 2]$$

where P = pairing energy to pair up electron.

Q.7 Calculate the paramagnetism into following compound ?



Ans. In all compound H_2O is a weak field ligand so pairing of electron will not occur in

(I) $[Cr(H_2O)_6]^{3+}$ (II) $[Fe(H_2O)_6]^{3+}$ (III) $[Zn(H_2O)_6]^{2+}$

e_g^0		e_g^2		e_g^4	
t_{2g}^3		t_{2g}^3		t_{2g}^6	
$n = 3$	$n = 5$		$n = 0$		

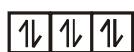
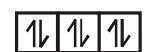
$$\mu = \sqrt{15}$$

$$\mu = \sqrt{35}$$

$$\mu = 0$$

Q.8 Why the d^8 configuration always shows paramagnetism 2.83 B.M in octahedral complex?

Ans. In given d^8 configuration for octahedral complex for both strong field ligand and weak field ligand is always have two unpaired electron.



Strong field ligand

$$n = 2$$

Weak field ligand

$$n = 2$$

$$\mu = \sqrt{n(n+2)} \text{ B.M.} = \sqrt{2(2+2)} = 2.83 \text{ B.M.}$$



EXERCISE-I (Conceptual Questions)

TERMINOLOGY OF COORDINATION COMPOUND

- In the complex ion $[\text{Fe}(\text{EDTA})]^-$ the coordination number and oxidation state of central metal ion is :-
 - C. N. = 6 O. N. = +3
 - C. N. = 1 O. N. = -1
 - C. N. = 4 O. N. = +2
 - C. N. = 3 O. N. = +3
- The coordination number and oxidation number of the central metal ion in the complex $[\text{Pt}(\text{en})_2]^{+2}$ is :-
 - C. N. = 2, O. N. = +2
 - C. N. = 6, O. N. = +4
 - C. N. = 4, O. N. = +4
 - C. N. = 4, O. N. = +2
- Select bidentate or didentate ligand from the following.

(1) CO	(2) SCN^-
(3) CH_3COO^-	(4) $\text{C}_2\text{O}_4^{2-}$
- The oxidation and coordination number of Pt in $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ is respectively :-

(1) + 1, 3	(2) + 2, 4
(3) + 3, 6	(4) + 2, 5
- The CN and ON of X in the compound $[\text{X}(\text{SO}_4)_2(\text{NH}_3)_5]^-$ will be :-

(1) 10 and 3	(2) 1 and 6
(3) 6 and 4	(4) 6 and 2
- What is the oxidation number of Fe in $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$ ion?

(1) +2	(2) +3	(3) +1	(4) 0
--------	--------	--------	-------
- The oxidation state of iron in $\text{Na}_4[\text{Fe}(\text{CN})_5(\text{NOS})]$ is

(1) +1	(2) +2	(3) +3	(4) zero
--------	--------	--------	----------
- Incorrect statement about DMG:-

(1) It is tetradentate ligand
(2) Chelating ligand
(3) dioxime of diacetyl
(4) in gravimetric determination of Ni is used

IUPAC - NOMENCLATURE

- $\text{K}_3[\text{Fe}(\text{CN})_6]$ is :-
 - Potassium hexacyano ferrate (II)
 - Potassium hexacyano ferrate (III)
 - Potassium ferri-cyanide
 - Hexacyano ferrate (III) potassium

Correct answer is :-

 - Only (a) and (b)
 - Only (b) and (c)
 - Only (a) and (c)
 - Only (b) and (d)
- The IUPAC name of $\text{K}_2[\text{Cr}(\text{CN})_2\text{O}_2(\text{O})_2(\text{NH}_3)]$ is :-
 - Potassium amminedicyano dioxoperoxochromate(VI)
 - Potassium amminecyanoperoxodioxo chromium (VI)
 - Potassium amminecyanoperoxodioxo chromium (VI)
 - Potassium amminecyanoperoxodioxo chromate (IV)
- The IUPAC name for $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ is :-
 - Hexaammine cobalt (III) hexacyanochromate (III)
 - Hexacyanochromium cobalt hexaammine (VI)
 - Hexaammine cobalt (III) hexacyanochromium (VI)
 - Hexacyanochromium (III) hexaammine cobalt (III)



18. The IUPAC name for $[\text{Co}(\text{NCS})(\text{NH}_3)_5]\text{Cl}_2$ is :-
(1) Pentaammine (thiocyanato-N) cobalt (III) chloride
(2) Pentaammine (thiocyanato-S) cobalt (III) chloride
(3) Pentaammine (isothiocyanato-N,S)cobalt (III) chloride
(4) Pentaammine (mercapto-N) cobalt (III) chloride

19. IUPAC name of $\text{K}_2[\text{OsCl}_5\text{N}]$ will be
(1) Potassium pentachloroazido osmate (VIII)
(2) Potassium pentachloroazido osmate (VI)
(3) Potassium pentachloro nitrido osmate (VI)
(4) Potassium nitro osmate (III)

WERNER'S THEORY & EAN

20. Which of the following has least conductivity in aqueous solution.
 (1) $\text{Co}(\text{NH}_3)_4\text{Cl}_3$ (2) $\text{Co}(\text{NH}_3)_3\text{Cl}_3$
 (3) $\text{Co}(\text{NH}_3)_5\text{Cl}_3$ (4) $\text{Co}(\text{NH}_3)_6\text{Cl}_3$

21. If EAN of a central metal ion X^{+2} in a complex is 34. and atomic number of X is 28. The number of monodentate ligands present in complex are:-
 (1) 3 (2) 4 (3) 6 (4) 2

22. The EAN of cobalt in the complex ion $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ is :-
 (1) 27 (2) 36 (3) 33 (4) 35

23. The effective atomic number of Cr (atomic no. 24) in $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ is
 (1) 35 (2) 27 (3) 33 (4) 36

24. Which gives only 25% mole of AgCl , when reacts with AgNO_3 :-
 (1) $\text{PtCl}_2 \cdot 4\text{NH}_3$ (2) $\text{PtCl}_4 \cdot 5\text{NH}_3$
 (3) $\text{PtCl}_4 \cdot 4\text{NH}_3$ (4) $\text{PtCl}_4 \cdot 3\text{NH}_3$

25. In the metal carbonyls of general formula $\text{M}(\text{CO})_x$ (Which follows EAN rule) if M is Ni, Fe and Cr the value of x will be respectively:-
 (1) 6, 5, 6 (2) 4, 5, 6
 (3) 4, 4, 5 (4) 4, 6, 6

26. A compound has the empirical formula $\text{CoCl}_3 \cdot 5\text{NH}_3$. When an aqueous solution of this compound is mixed with excess silver nitrate, 2 mol of AgCl precipitate per mol of compound. On reaction with excess HCl , no NH_4^+ is detected. Hence it is
 (1) $\text{Co}(\text{NH}_3)_5\text{Cl}_2\text{Cl}$
 (2) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
 (3) $[\text{Co}(\text{NH}_3)_5\text{Cl}_3]$
 (4) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{NH}_3$

27. Which of the following pair the EAN of central metal atom is not same?
 (1) $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{NH}_3)_6]^{3+}$
 (2) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ and $[\text{Cr}(\text{CN})_6]^{3-}$
 (3) $[\text{FeF}_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$
 (4) $[\text{Ni}(\text{CO})_4]$ and $[\text{Ni}(\text{CN})_4]^{2-}$

VALENCE BOND THEORY

28. Which of the following compound is paramagnetic
 (1) Tetracyanonickelate (II) ion
 (2) Tetraamminezinc (II) ion
 (3) Hexaamine chromium (III) ion
 (4) Diammine silver (I) ion

29. The shape of the complex $[\text{Ag}(\text{NH}_3)_2]^+$ is :
 (1) Octahedral (2) Square planar
 (3) Tetrahedral (4) Linear

30. Hexafluoroferrate (III) ion is an outer orbital complex. The number of unpaired electrons are
 (1) 1 (2) 5
 (3) 4 (4) Unpredictable

31. The shape of $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ is :
 (1) Square planar (2) Pyramidal
 (3) Octahedral (4) Tetrahedral

32. Among the following ions, which one has the highest paramagnetism ?
 (1) $[\text{FeF}_6]^{3-}$ (2) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
 (3) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ (4) $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$

33. In the complex ion ML_6^{n+} , M^{n+} has five d-electrons and L is weak field ligand. According to crystal field theory, the magnetic properties of the complex ion correspond to how many unpaired electrons
 (1) 0 (2) 5 (3) 2 (4) 3

34. A magnetic moment of 1.73 BM will be shown by one among of the following compounds .
 (1) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ (2) $[\text{Ni}(\text{CN})_4]^{2-}$
 (3) TiCl_4 (4) $[\text{CoCl}_6]^{3-}$

35. The magnetic property and the shape of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ complex ions are :
 (1) Paramagnetic, Octahedral
 (2) Diamagnetic, square planar
 (3) Paramagnetic, tetrahedral
 (4) None of the above

36. Amongst the following ions which one has the highest paramagnetism
 (1) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ (2) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
 (3) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ (4) $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$

37. Which of the following complexes is an inner orbital complex ?
 (1) $[\text{CoF}_6]^{3-}$ (2) $[\text{FeF}_6]^{3-}$
 (3) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ (4) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

38. The wrong statement is :-
 (1) Halide ligands forms high spin complex
 (2) Strong ligands form low spin complex
 (3) $[\text{FeF}_6]^{3-}$ is inner orbital complex
 (4) $[\text{NiCl}_4]^{2-}$ is outer orbital complex

39. What is Incorrect for $K_4[Fe(CN)_6]$
 (1) O.N of Iron is +2
 (2) It exhibit diamagnetic character
 (3) It exhibit paramagnetic character
 (4) It involved d^2sp^3 hybridisation

40. In which of the following molecules, central atom used orbitals of different principle quantum number in the hybridisation :-
 (1) $[Fe(CO)_5]$ (2) IF_7
 (3) $Ni(CO)_4$ (4) XeO_4

41. What are the geometric shape and the oxidation number of the copper atom, respectively, for the complex ion, $[Cu(NH_3)_4(OH_2)_2]^{2+}$?
 (1) Tetrahedral; + 2
 (2) Square planar; - 2
 (3) Linear; + 3
 (4) Octahedral; + 2

42. For FeF_6^{3-} and $Fe(CN)_6^{3-}$ magnetic moment of the fluoride complex is expected to be:-
 (1) The same as the magnetic moment of the cyanide complex
 (2) Larger than the magnetic moment of the cyanide complex because there are more unpaired electrons in the fluoride complex
 (3) Smaller than the magnetic moment of the cyanide complex because there are more unpaired electrons in the fluoride complex
 (4) Larger than the magnetic moment of the cyanide complex because there are fewer unpaired electrons in the fluoride complex

43. Which of the following contains one unpaired electron in the 4p orbitals :-
 (1) $[Cu(NH_3)_2]^+$ (2) $[Cu(NH_3)_4]^{2+}$
 (3) $[Cu(CN)_4]^{3-}$ (4) $[Ni(CN)_4]^{2-}$

44. Which of the following complexes are low spin and diamagnetic?
 (a) $K_4[Os(CN)_6]$
 (b) $[Mo(CO)_6]$
 (c) $[Mn(CN)_6]^{4-}$
 Select the correct answer using the codes given below:
 (1) a, b and c (2) a and b only
 (3) a and c only (4) b and c only

45. How many unpaired electrons are present in the Brown Ring complex $[Fe(H_2O)_5(NO)]SO_4$
 (1) 4 (2) 3
 (3) 0 (4) 5

46. Which of the following statements about $Fe(CO)_5$ is correct?
 (1) It is paramagnetic and high spin complex
 (2) It is diamagnetic and high spin complex
 (3) It is diamagnetic and low spin complex
 (4) It is paramagnetic and low spin complex

47. Which is true for $[Ni(en)_2]^{2+}$, $Z(Ni) = 28$?
 (1) paramagnetism, dsp^2 , square planar, C.N. of Ni = 2
 (2) diamagnetism, dsp^2 , square planar, C.N. of Ni = 4
 (3) diamagnetism, sp^3 , tetrahedral, C.N. of Ni = 4
 (4) paramagnetism, sp^3 , tetrahedral, C.N. of Ni = 4

48. Arrange the following in order of decreasing number of unpaired electrons:
 I : $[Fe(H_2O)_6]^{2+}$ II : $[Fe(CN)_6]^{3-}$
 III : $[Fe(CN)_6]^{4-}$ IV : $[Fe(H_2O)_6]^{3+}$
 (1) IV, I, II, III (2) I, II, III, IV
 (3) III, II, I, IV (4) II, III, I, IV

CFT, COLOUR OF THE COMPLEX AND STABILITY

49. Which one of these ions absorbs energy from visible spectrum :-
 (1) $[Cu(NH_3)_4]^{2+}$ (2) $[Cu(NH_3)_4]^{+2}$
 (3) $[Zn(H_2O)_6]^{2+}$ (4) $[Co(H_2O)_6]^{+3}$

50. In the complex $[Ni(H_2O)_2(NH_3)_4]^{+2}$ the magnetic moment (μ) of Ni is :-
 (1) Zero (2) 2.83 BM
 (3) 1.73 BM (4) 3.87 BM

51. Which of the following system has maximum number of unpaired electrons :-
 (1) d^5 (Octahedral, low spin)
 (2) d^8 (Tetrahedral)
 (3) d^6 (Octahedral, low spin)
 (4) d^3 (Octahedral)

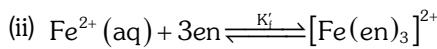
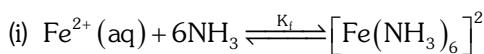
52. In an octahedral crystal field, the t_{2g} orbitals are
 (1) Raised in energy by $0.4 \Delta_0$
 (2) Lowered in energy by $0.4 \Delta_0$
 (3) Raised in energy by $0.6 \Delta_0$
 (4) Lowered in energy by $0.6 \Delta_0$

53. If $\Delta_0 < P$, the correct electronic configuration for d^4 system will be :-
 (1) $t_{2g}^4 e_g^0$ (2) $t_{2g}^3 e_g^1$
 (3) $t_{2g}^0 t_g^4$ (4) $t_{2g}^2 e_g^2$

54. Match List-I (Complex ions) with List-II (Number of Unpaired Electrons) and select the correct answer using the codes given below the lists :-

List -I (Complex ions)		List II (Number of Unpaired Electrons)			
Code :	A	B	C	D	
(1)	iv	i	ii	v	
(2)	ii	v	iii	i	
(3)	iv	v	ii	i	
(4)	ii	i	iii	v	

55. Consider the following complex formation reactions and comment on their formation constant value



(1) $K_f > K'_f$ (2) $K_f < K'_f$
(3) $K_f = K'_f$ (4) can not be compared

56. Select most stable complex :-

(1) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ (2) $[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{+3}$
(3) $[\text{Co}(\text{en})_3]^{+3}$ (4) $[\text{Co}(\text{NH}_3)_4(\text{en})]^{+3}$

57. What will be the theoretical value of 'spin only' magnetic moment when $\text{Fe}(\text{SCN})_3$ reacts with a solution containing F^- ions to yield a complex ?

(1) 2.83 B.M. (2) 3.87 B.M.
(3) 5.92 B.M. (4) 1.73 B.M.

58. Which one of the following high-spin complexes has the largest CFSE (Crystal field stabilization energy)?

(1) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ (2) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
(3) $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ (4) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

59. Match List-I (Complex ions) with List-II (CFSE) and select the correct answer using the codes given below the lists :

Column-I		Column-II			
(P) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	(Q) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	1. $0.6 \Delta_0$	2. $0.4 \Delta_0$	3. 0	4. $1.2 \Delta_0$
P	Q	R	S		
(1) 3	1	2	4		
(2) 1	2	3	4		
(3) 4	3	2	1		
(4) None of these					

ISOMERISM

60. A square planar complex is cis platin $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, shows :
(1) Geometrical isomerism (2) Optical isomerism
(3) Linkage isomerism (4) None

61. The two compounds sulphato penta-ammine cobalt (III) bromide and sulphato penta-ammine cobalt (III) chloride represent :
(1) Linkage isomerism
(2) Ionisation isomerism
(3) Co-ordination isomerism
(4) No isomerism

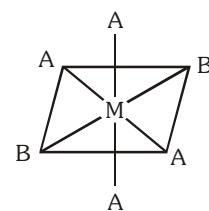
62. Which of the following complex can not exhibit geometrical isomerism :-
(1) $[\text{Pt}(\text{NH}_3)_2\text{Cl} \text{NO}_2]$ (2) $[\text{Pt}(\text{gly})_2]$
(3) $[\text{Cu}(\text{en})_2]^{+2}$ (4) $[\text{Pt}(\text{H}_2\text{O})(\text{NH}_3)\text{BrCl}]$

63. Which one of the following compounds will exhibit linkage isomerism :-
(1) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ (2) $[\text{Co}(\text{NH}_3)_3 \text{NO}_2]\text{Cl}_2$
(3) $[\text{Co}(\text{NH}_3)_4 \text{Cl}_2]\text{Cl}$ (4) $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$

64. Out of the following which complex will show geometrical isomerism ?
(1) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ (2) $\text{Ni}(\text{CO})_4$
(3) $\text{Na}_3[\text{Ni}(\text{CN})_4]$ (4) $\text{K}[\text{Ag}(\text{CN})_2]$

65. Which of the following complexes will show optical isomerism ?
(1) $[\text{Cr}(\text{NH}_3)_6]^{2+}$ (2) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
(3) $[\text{Pt}(\text{NH}_3)_3\text{Br}]\text{NO}_3$ (4) $[\text{Cr}(\text{en})_3]\text{Cl}_3$

66. The compound $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ represent
(1) Linkage isomerism
(2) Hydration isomerism
(3) Ligand isomerism
(4) None of these



67. The isomer -

can be marked as -

(1) Cis isomer (2) Leavo isomer
(3) Dextro isomer (4) Trans isomer



68. A Planar Complex (Mabcd) gives :-
 (1) Two Optical isomer
 (2) Two geometrical isomer
 (3) Three optical isomer
 (4) Three geometrical isomers

69. Theoretically the No. of geometrical isomers expected for octahedral complex [Mabcdef] is:-
 (1) Zero (2) 30 (3) 15 (4) 9

70. Which of the following complex produce ppt with AgNO_3 and exist in two geometrical isomeric form
 (1) $\text{PtCl}_2 \cdot 4\text{NH}_3$ (2) $\text{PtCl}_2 \cdot 3\text{NH}_3$
 (3) $\text{PtCl}_4 \cdot 4\text{NH}_3$ (4) $\text{PtCl}_4 \cdot 2\text{NH}_3$

71. Cis[Pt(en)₂Cl₂]Br₂.2H₂O and trans[Pt(en)₂Br₂]Cl₂.2H₂O are :-
 (1) Ionisation isomer
 (2) Geometrical isomer
 (3) Hydrate isomer
 (4) None of these

72. Which of the following octahedral complex have maximum stereoisomers :-
 (1) $[\text{M}(\text{CN})_6]^\pm$ (2) $[\text{M}(\text{en})(\text{CN})_4]^\pm$
 (3) $[\text{M}(\text{en})_2(\text{CN})_2]^\pm$ (4) $[\text{M}(\text{en})_3]^\pm$

73. Which of the following complex does no show geometrical isomerism ?
 (1) $[\text{Co}(\text{NH}_3)_4 \text{Cl}_2]^\pm$ (2) $[\text{Co}(\text{NH}_3)_3 (\text{NO}_2)_3]^\pm$
 (3) $[\text{Cr}(\text{en})_3]^{3+}$ (4) $[\text{Pt}(\text{gly})_2]^\pm$

74. Select the correct statement :
 (1) Potassium ferrocyanide and potassium ferricyanide can be differentiated by measuring the solid state magnetic moment.
 (2) The complex $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ can be differentiated by adding aqueous solution of barium chloride
 (3) The complex $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}$ and $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}$ can be differentiated by adding aqueous solution of silver nitrate.
 (4) All of these

75. Which of the following complex compounds does not exhibits geometrical isomerism ?
 (1) $[\text{PtCl}_2(\text{NH}_3)_2]^\pm$ (2) $[\text{PdCl}_2\text{Br}]^\pm$
 (3) $[\text{Pt}(\text{NH}_3)(\text{py})(\text{Cl})(\text{Br})]^\pm$ (4) $[\text{Pt}(\text{NH}_3)_3(\text{Br})]^\pm$

76. The pair of molecules that exhibit geometrical isomerism are
 (1) $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^\pm$ and $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^\pm$
 (2) $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$
 (3) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$
 (4) All of the above show geometric isomerism

ORGANOMETALLIC COMPOUNDS

77. Which of the following is π -acid ligand
 (1) NH_3 (2) CO
 (3) gly. (4) ethylene diamine

78. Which of the following statement is/are wrong:-
 (a) Al_4C_3 is an organometallic compound
 (b) Metal carbonyls are organometallic compounds
 (c) TEL is π bonded organometallic compound
 (d) Frankland reagent is σ - bonded organometallic compound
 The answer is:-
 (1) c and d (2) a and c
 (3) a and b (4) All are correct

79. Compounds which contain one or more metal carbon bonds are called :
 (1) Organic compound (2) Complex compound
 (3) Metal carbides (4) OMC compounds.

80. Which one of the following is used as a heterogeneous catalyst ?
 (1) Wilkinson's catalyst (2) Tetraethyl lead
 (3) Zeigler Natta catalyst (4) Grignard's reagent

81. Which of the following statement is true
 (1) FeCO_3 and Fe_3C are organometallic compounds.
 (2) In ferrocene ligand is cyclopentadienyl.
 (3) $\text{Pb}(\text{C}_2\text{H}_5)_4$ is π -bonded OMC
 (4) In zeise salt central metal is Sp^3 hybridised.

82. Synergic bonding involves :-
 (1) The transference of electrons from ligands to metal
 (2) The transference of electrons from filled metal orbitals to anti-bonding orbitals of ligands
 (3) Both the above
 (4) None of these

83. OMC form during purification of a metal is :-
 (1) $\text{Ni}(\text{CO})_4$ (2) $\text{Pb}(\text{C}_2\text{H}_5)_4$
 (3) $\text{Li-C}_4\text{H}_9$ (4) $\text{Na}_2[\text{Ni}(\text{CN})_4]$

84. Which of the following is not an organo metallic compound :-
 (1) $(\text{C}_2\text{H}_5)_2\text{Zn}$ (2) $\text{CH}_3\text{B}(\text{OCH}_3)_2$
 (3) $\text{B}(\text{OCH}_3)_3$ (4) $\text{Ni}(\text{CO})_4$

APPLICATION OF COORDINATION CHEMISTRY

85. The brown ring test for nitrites and nitrates is due to the formation of a complex ion with formula :-
 (1) $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ (2) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
 (3) $[\text{Fe}(\text{H}_2\text{O})(\text{NO})_5]^{2-}$ (4) $[\text{Fe}(\text{NO})(\text{CN})_5]^{2+}$

86. In a ferric salt on adding KCN a prussian blue is obtained which is :-
 (1) $\text{K}_3[\text{Fe}(\text{CN})_6]$ (2) $\text{Fe}_3[\text{Fe}(\text{CN})_6]_4$
 (3) $\text{FeSO}_4[\text{Fe}(\text{CN})_6]$ (4) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$



EXERCISE-I (Conceptual Questions)

ANSWER KEY



EXERCISE-II (Assertion & Reason)

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

(A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
(B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
(C) If Assertion is True but the Reason is False.
(D) If both Assertion & Reason are false.

1. **Assertion:** The aqueous solution of $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ is acidic in nature.
Reason : It ionises to give a complex ion.
(1) A (2) B (3) C (4) D

2. **Assertion :** In the complex $K_2[PtCl_6]$, coordination number of Pt is 6.
Reason : In the complex six coordinate bonds are formed between Pt and chloro ligands.
(1) A (2) B (3) C (4) D

3. **Assertion :** Tetrahedral complex do not exhibit geometrical isomerism.
Reason : In tetrahedral complex all the four positions are identical.
(1) A (2) B (3) C (4) D

4. **Assertion :** $[Fe(CO)_5]$ is inner orbital complex.
Reason : In the given complex oxidation state of Iron is zero.
(1) A (2) B (3) C (4) D

5. **Assertion :** $[Fe(CN)_6]^{4-}$ is paramagnetic in nature.
Reason : $[Fe(CN)_6]^{4-}$ is low spin complex.
(1) A (2) B (3) C (4) D

6. **Assertion :** Hexachloroplatinate is a complex anion.
Reason: Complex has negatively charged ligands
(1) A (2) B (3) C (4) D

7. **Assertion :** $[Ni(CN)_4]^{2-}$ has zero unpaired electron while that of $[NiCl_4]^{2-}$ has two unpaired e^-
Reason: $[Ni(CN)_4]^{2-}$ has strong crystal field while $[NiCl_4]^{2-}$ has weak crystal field
(1) A (2) B (3) C (4) D

8. **Assertion :** Cis - $[Fe(en)_2Cl_2]^+$ can form racemic mixture.
Reason : Cis - $[Fe(en)_2Cl_2]^+$ is square planar complex .
(1) A (2) B (3) C (4) D

9. **Assertion:** Square planar complex Ma_2b_2 has two optical isomers
Reason : Mirror image of Ma_2b_2 is non-superimposable.
(1) A (2) B (3) C (4) D

10. **Assertion :** AgI is coloured while AgF is colourless.
Reason : Unpaired e^- is present in AgI
(1) A (2) B (3) C (4) D

11. **Assertion :** $[CoF_6]^{3-}$ is high spin complex.
Reason : F^- is strong field ligand.
(1) A (2) B (3) C (4) D

12. **Assertion :** Ferrocene is π -bonded organometallic compound.
Reason : Ferrocene is a sandwich compound.
(1) A (2) B (3) C (4) D

13. **Assertion :** Solution of Na_2CrO_4 in water is intensely coloured.
Reason: Ox. state of Cr in Na_2CrO_4 is +6.
(1) A (2) B (3) C (4) D

14. **Assertion :** Potassium ferrocyanide is diamagnetic whereas potassium ferricyanide is paramagnetic.
Reason : Crystal field splitting in ferrocyanide ion is greater than that of ferricyanide ion.
(1) A (2) B (3) C (4) D

15. **Assertion :-** In a mixture of $Cd(II)$ and $Cu(II)$, (Cd^{2+}) gets precipitated in presence of KCN by H_2S .
Reason :- The stability constant of $[Cu(CN)_4]^{4-}$ is greater than $[Cd(CN)_4]^{2-}$
(1) A (2) B (3) C (4) D

16. **Assertion :-** aq. solution of $CoCl_2$ is pink in colour. It turns blue in presence of conc. HCl .
Reason :- It is due to formation of $(CoCl_4)^{2-}$.
(1) A (2) B (3) C (4) D



17. Assertion : Triethylenediamine is a bidentate monoanion.
Reason : Complex containing propylenediamine ligand shows ligand isomerism.
(1) A (2) B (3) C (4) D

18. Assertion : $[\text{Co}^{\text{III}}(\text{gly})_3]$ is called inner-metallic complex because,
Reason : Both the coordination number and charge of the cation are satisfied simultaneously by ligands.
(1) A (2) B (3) C (4) D

19. Assertion : All tetrahedral complexes are mainly high spin and the low spin configurations are rarely observed.
Reason: Δ_t is always much smaller even with stronger field ligands and it is never energetically favourable to pair up the electrons.
(1) A (2) B (3) C (4) D

20. Assertion : NH_2NH_2 although possesses two electron pairs for donation but not acts as a chelating agent.
Reason: The coordination by NH_2NH_2 leads to a three member highly unstable strained ring
(1) A (2) B (3) C (4) D

21. Assertion : The correct order for the wave length of absorption in the visible region is ; $[\text{Ni}(\text{NO}_2)_6]^{4-} < [\text{Ni}(\text{NH}_3)_6]^{2+} < [\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
Reason: The stability of different complexes depends on the strength of the ligand field of the various ligands.
(1) A (2) B (3) C (4) D

22. Assertion : The 'spin only' magnetic moment of a green complex, potassium amminetetracyanodinitrosonium chromate(I) is 1.73 BM.
Reason : To have two d-orbitals empty for $d^2\text{sp}^3$ hybridisation, the pairing of electrons take place leaving behind one unpaired electron as CN^- is a stronger ligand.
(1) A (2) B (3) C (4) D

23. Assertion : Pentaamminethiocyanato-N-chromium(III) tetrachloridozincate(II) is a coloured compound and is an example of ionisation isomerism.
Reason : The compound is paramagnetic and therefore, d-d transition is possible
(1) A (2) B (3) C (4) D

24. Assertion :- $\text{Cu}[\text{Hg}(\text{SCN})_4]$ and $\text{Hg}[\text{Co}(\text{NCS})_4]$ are isomers.
Reason :- SCN^- is an ambidentate ligand.
(1) A (2) B (3) C (4) D

25. Assertion :- Coordination number of Pt in Zeise's salt is 5.
Reason :- C_2H_4 act as bidentate ligand
(1) A (2) B (3) C (4) D

26. Assertion :- Fe^{+3} not used in brown ring test of NO_3^- .
Reason :- NO_3^- is first converted into NO_2 .
(1) A (2) B (3) C (4) D

27. Assertion : $[\text{Co}(\text{H}_2\text{O})_6]^{+3} \rightarrow [\text{Co}(\text{H}_2\text{O})_6]^{+2}$ changes its colour on reduction.
Reason : Crystal field stabilisation energy increases on reduction
(1) A (2) B (3) C (4) D

28. Assertion :- Zone refining is based on the fact that impurities are more soluble in molten state than in solid in the presence of oxygen.
Reason :- This method is used to prepare pure metal oxides.
(1) A (2) B (3) C (4) D

29. Assertion :- If in $[\text{Co}(\text{NH}_3)_6]^{+3}$, NH_3 is replaced by H_2O , same wavelength will be absorbed by the complex :
Reason :- It is a high spin species.
(1) A (2) B (3) C (4) D

EXERCISE-II (Assertion & Reason)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	1	1	2	2	2	1	3	4	3	3	2	2	3	1
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	
Ans.	1	4	2	1	1	2	1	4	4	4	3	3	4	4	

